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ORIGINAL PAPER

Hybrid organic/inorganic films of conducting polymers modified with phthalocyanines. I—Film preparation and voltammetric studies

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Abstract Conducting polymers were deposited on the surface of platinum and glassy carbon electrodes. The monomers used were *N*-methyl pyrrole and 3-methyl thiophene. The electrochemical synthesis of the polymer was achieved using constant applied potential or cyclic polarization techniques in acetonitrile as a solvent and tetra-alkyl ammonium salts as supporting electrolyte. The resulting conducting polymeric film was modified with an inorganic metal complex, namely, Cu–phthalocyanine or Co–phthalocyanine. Two different approaches were adopted for the modification: (1) the first was to directly apply the metal–phthalocyanine layer on the surface of the polymer, and (2) the second was by the inclusion of the metal–phthalocyanine in a sol–gel matrix that was in turn applied to the conducting polymer film. In the first part of this work, we studied the effect of changing the type of polymer matrix and the central metal of the inorganic complex on the electrochemical behavior of the resulting film. We also found that changing the method of metal–phthalocyanine application to the polymer film affected the electrochemical response and kinetics at the electrode surface. The new electrode was tested for the reduction of hydrogen peroxide and showed better conversion efficiency compared to conventional surfaces, which suggests its use in fuel cell applications.

Keywords Conducting polymers · Metal–phthalocyanines · Hybrid organic/inorganic composites · Voltammetry · Fuel cells

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Introduction

The presence of extended conjugated π-electron is of foremost importance in conductive polymers. This class of polymers may be synthesized using the standard methods of polymerization including conventional as well as specific routes which include Witting, Horner, and Grignard reactions, polycondensation processes, and metal-catalyzed polymerization techniques [1–4]. Conductive polymers may also be synthesized by one of the following techniques: (1) electrochemical polymerization, (2) solid-state polymerization, (3) photochemical polymerization, and (4) pyrolysis. Simonet and Rault-Berthelot [5] reported that one uses electrochemistry for the direct formation of electrocrystals; a basic example is the oxidation of tetrathiafulvalene leading to mixed valence salts. Therefore, electrochemistry may, in some cases, produce and organize in a certain manner molecules and macromolecules at a solid conducting interface. This fact leads to be good tools for the direct synthesis of most of those materials and the study of their polymerization and doping processes. Moreover, these materials are currently used in various fields such as batteries, electronic devices, electrochromism, and modified electrodes.

The electropolymerization of different monomers resulted in different polymers with distinctive properties, namely, conjugation length and, consequently, the intrinsic dc conductivity of the polymer as was suggested by Roncali et al. [6].

On the other hand, the nature of the substrate on the surface potential of conducting polymer films affected the average value and the distribution of surface potential across the polymer surface [7].

Hybrid inorganic–organic materials, on the other hand, have extraordinary properties based on the combination of

the different building blocks [8]. Inorganic complexes were successfully incorporated in conducting polymer matrices and resulted in enhanced electron transfer rate at the modified surface/electrolyte interface [9, 10]. Metal (II) phthalocyanines (MPcs) are planar complexes, and they are of great technological and fundamental interest because of their unique optical and electrical properties. The MPcs are extensively used as pigments and dyes, and they are models for biologically important species such as porphyrins, hemoglobin, and chlorophyll. They can serve as the active elements in chemical sensors, especially for the detection of NO_2 [11]. Phthalocyanines are also well known as photoconductors in which they have conjugate bonds that can absorb light on either side of blue–green region in the visible spectrum. For example, poly(aniline) has conjugate bonds and is photosensitive, and when the thin films of this polymer are prepared with Co–phthalocyanine (CoPc) powder, the magnitude of absorption of the films not only increases but also broadens [12]. Therefore, CoPc is used in solar cells made of conducting polymers to increase their current conversion efficiency. The incorporation of some MPc oligomers was successfully achieved by electrochemical polymerization of pyrrole and aniline in aqueous media using sodium salt of MPc oligomer possessing carboxyl terminals as the supporting electrolyte [13]. The oligomeric MPc incorporated with poly(pyrrole) indicated stable and reversible electrochemical behavior in aqueous KCl media.

Several issues still need to be addressed regarding the hybrid structures of organic conducting polymers and MPcs. In this work, two different conducting polymeric systems will be tested for use as underlying layer for the application of the complex inorganic layer. Different methods for the application of the inorganic moieties containing MPc to the polymer structure will be used. The electrochemical behavior of the resulting new hybrid films will be compared to that of the unmodified polymer surface. In the second part of this work (Galal et al., submitted for publication), we will present the electrochemical spectroscopy results, structural characterization, and surface measurements of these films.

Experimental

Chemicals and reagents

All chemicals were used without further purification. 3-Methylthiophene (MT), *N*-methyl pyrrole (NMPY), tetrabutyl ammonium tetrafluoroborate (TBATFB), and tetraethyl ammonium tetrafluoro methyl sulfonate (TEATFMS), acetonitrile (AcN), tetraethylorthosilicate (TEOS), ferric nitrate, and potassium ferricyanide were obtained from Aldrich (Milwaukee, USA). Other chemicals were purchased from Merk (Munich, Germany). Aqueous solutions were prepared by dilution from stock solutions using double-distilled water.

Electrochemical cells and electrode materials

Electrochemical polymerization and characterizations were carried out with a three-electrode/one-compartment glass cell. The working electrode was a platinum (Pt) disk (radius: 1.5 mm) or a glassy carbon (GC) disk (radius: 3.0 mm). The auxiliary electrode was in the form of 2.0×2.0 cm^2 sheet or 6.0-cm-long wire. All potentials in this study were referenced to 3 M Ag/AgCl. All working electrodes were mechanically polished using an alumina (2 μm)/water slurry until no visible scratches were observed. Before immersion in the cell, the electrode surface was thoroughly rinsed with distilled water and dried. Highly purified nitrogen was used for oxygen removal by bubbling. All experiments were performed at 25±0.2 °C.

Equipment and techniques

The electrosynthesis of the polymers and their electrochemical characterization were performed using a BAS-100B electrochemical analyzer (BAS, West Lafayette, USA). The polymer films were electrochemically deposited by applying a constant potential on the working electrode for a given time or by repeatedly cycling the potential between two limits as will be indicated in the "Results and discussion" section. The thickness of the films was controlled by the amount of charge consumed for the electropolymerization (assuming 100% efficiency during the electrochemical conversion). From the SEM measurements (Galal et al., submitted for publication), the film thickening due to the sol–gel (including the inorganic complex) does not exceed few Angstroms.

Phthalocyanine application to the polymer

Polymer film modification was achieved mainly by two methods. In the first method, MPc was applied to the polymer film according to the following steps: a Co– or Cu–Pc solution (1.0×10^{-3} M) in 1 M $CCl_3COOCH/CHCl_3$ was prepared and stored at 0 °C to avoid decomposition. On a flat watch glass, few microliters of the clear deep-green Co–Pc or deep-blue Cu–Pc solution was continuously dropped into a 0.1-M aqueous NaOH solution (subphase). Relatively rigid and homogeneous film islands of Co–Pc/or Cu–Pc were formed on the superficial layer of the solution. The electrode surface was swapped horizontally over the thin film of the MPc. A layer of the MPc was thus applied on the electrode surface, rinsed with distilled

water, and left in air to dry. In the second method, Fe_2O_3/SiO_2 coating, or Fe_2O_3/SiO_2–phthalocyanine layer, was embedded to the polymer film. This method adopts the dip-coating technique of the polymer in a preprepared solution. This solution was prepared by mixing the following: 10% $FeCl_2$, formamide, ethanol, and 0.1 M nitric acid. The mixture was stirred for 2 h at room temperature until a clear pale yellow color was obtained. The solution was then used for dip coating the electrode. In the case when Cu– or Co–Pc was mixed with this solution, an addition of 0.5 wt% of the solution was used. The inorganic hybrid component was added to the polymer film by the dip-coating technique; thus, the electrode covered with the polymer film was immersed vertically into the sol–gel solution and left for a given time. The whole film and the electrode were left to dry at room temperature and then introduced in a conventional oven set at 200 °C for a total period of 15 min. The inorganic coating underwent a sol–gel process with the TEOS as the inorganic precursor to produce the hybrid material with conducting polymer film. These methods of hybrid film preparation are fairly reproducible. Ten film preparations were compared for their corresponding electrochemical responses with CV. Less than 2% errors were obtained from the current values recorded.

Results and discussion

Electropolymerization of *N*-methyl pyrrole

Several electrochemical and physicochemical conditions have to be optimized to obtain a film with satisfactory properties by electrochemical polymerization. The most important property in this work is to obtain polymeric films with relatively high conductivity and compact morphology. This will allow better control for the modifying covering layer applied thereafter. Many variables were found to affect the properties of the polymer such as the nature/concentration of monomer, nature/concentration of supporting electrolyte, nature/purity/dryness of solvent, temperature of preparing solution, and electrochemical method used for the synthesis (Galal et al., submitted for publication). In this respect, two different types of supporting electrolytes and solvents were used in the electropolymerization, namely, TEATFMS in AcN and sulfuric acid in water. Figure 1a shows the repeated cyclic voltammograms for the formation of poly-NMPY (PNMPY) in TEATFMS/AcN. The potential limits for the repeated potential cycles applied to the working Pt electrode are E_i=−0.2 V and E_f=+1.8 V with a scan rate of 50 mV/s. As the number of cycles increases, the corresponding current increases in both the anodic and the cathodic part of the voltammogram in the ranges +1.0 to +1.8 V and +1.0 to 0.0 V, respectively. This is indicative of polymer film thickening and that its electrical conductivity is also pronounced.

On the other hand, when the potential limit is restricted, ca. between −0.2 and +1.2 V as depicted in Fig. 1b, the current increases in a more uniform way with relatively low value. However, the films obtained are more compact and adhere strongly to the Pt electrode. In this study, all PNMPY films formed using repeated cycles in the potential limit as in the previously mentioned restricted range for 10 cycles.

The effect of changing the supporting electrolyte and the solvent on the electrochemical synthesis of the polymer is shown in Fig. 1c. In this case, the supporting electrolyte used is 0.1 M sulfuric acid in water. Two important observations are noticed: (1) the overall current both in the cathodic and anodic portions of the cyclic voltammogram is relatively low, and (2) as the number of cycles

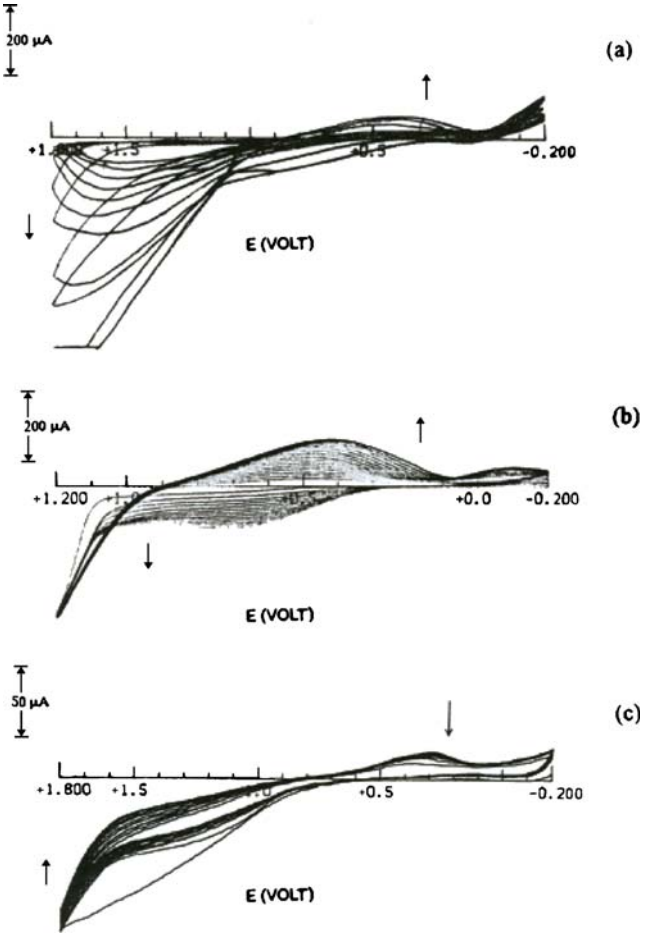

Fig. 1 **a** Repeated CVs (10 cycles) for the formation of PNMPY. Electrolyte: 0.05 M TEATFMS/AcN, Pt electrode, ν=50 mV/s (E_1=−0.2 V, E_2=+1.8 V). **b** Repeated CVs (10 cycles) for the formation of PNMPY (potential limit is restricted). Electrolyte: 0.05 M TEATFMS/AcN, Pt electrode, ν=50 mV/s, (E_1=−0.2 V, E_2=+1.2 V). **c** Repeated CVs (10 cycles) for the formation of PNMPY. Electrolyte: 0.1 M H_2SO_4/H_2O (E_1=−0.2 V, E_2=+1.8 V)

increases, the current tends to decrease. This is completely opposite to that observed in Fig. 1a. Moreover, the resulting polymer films formed in H_2SO_4 are rather fragile, non-adherent to the Pt substrate, and less conductive. Although oxygen evolution is possible at relatively high positive potentials reached in this measurement, however, gas evolution was not observed by eye inspection of the electrode surface. Film stability after exposure to this relatively positive potential did not affect its integrity that was confirmed from possible use of the film in subsequent experiments with no noticeable change in the current signal.

Electrochemical testing of poly(*N*-methyl pyrrole) and its modification with phthalocyanine films

Electrochemical testing of poly(N-methyl pyrrole)

The electrochemical behavior of a PNMPY film in 0.1 M KCl is given in Fig. 2a. The polymer was formed by repeated cycles (10 cycles, 100 mV/s) between −0.2 and +1.2 V in TBATFB. As would be expected for PNMPY films, no appreciable current is observed in the range between −0.2 and +1.0 V. In the forward (anodic) direction, the current starts to increase as the potential exceeds +1.1 V, and a peak appears at ca. +1.7 V. This indicates the oxidation (doping) of the polymer due to the anion exchange at the film/electrolyte interface. A small peak is observed in the reverse scan at ca. +1.05 V and a relatively broad one at −0.40 V. The first indicates partial undoping of the film, and the second is due to the completeness of the reduction process.

Modification of poly(N-methyl pyrrole) with phthalocyanine

The PNMPY film was formed by cycling as mentioned above and then modified by a CuPc layer according to the first method explained in the "Experimental" section. The Osteryoung square-wave voltammogram (OSWV) of this film in 0.1 M KCl is given in Fig. 2b. When the CuPc is dissolved in KCl test solution rather than incorporated in the polymer film, the corresponding OSWV for the unmodified PNMPY is shown in Fig. 2c. The two voltammograms display similar characteristics, namely, several peaks at ca. −0.18, −0.12, −0.05, +0.02, and +0.105 V. Multipeaks due to charge transfer at phthalocyanine films were reported earlier [15]. Also, as could be observed, the current is relatively small in this potential range as a result of the low conductivity of the film, and the insulation imparts to its surface by the thin phthalocyanine layer.

When the above PNMPY/CuPc hybrid film is covered with another PNMPY layer, the configuration becomes PNMPY/CuPc/PNMPY/electrolyte. This is achieved by electropolymerizing a layer of PNMPY over the PNMPY/CuPc film. The OSWV of this latter "composite" film in 0.1 M KCl is given in Fig. 2d. Most of the peaks disappear, and a single broad one is retained at −0.05 V that indicates partially controlled diffusion phenomena at this potential. The "outer" polymer layer acts as a barrier for charge transfer with the CuPc. It is important to mention that the thickness of the first layer of polymer (i.e., the system: Pt/polymer) is ca. 800 Å and that of the outer polymer layer

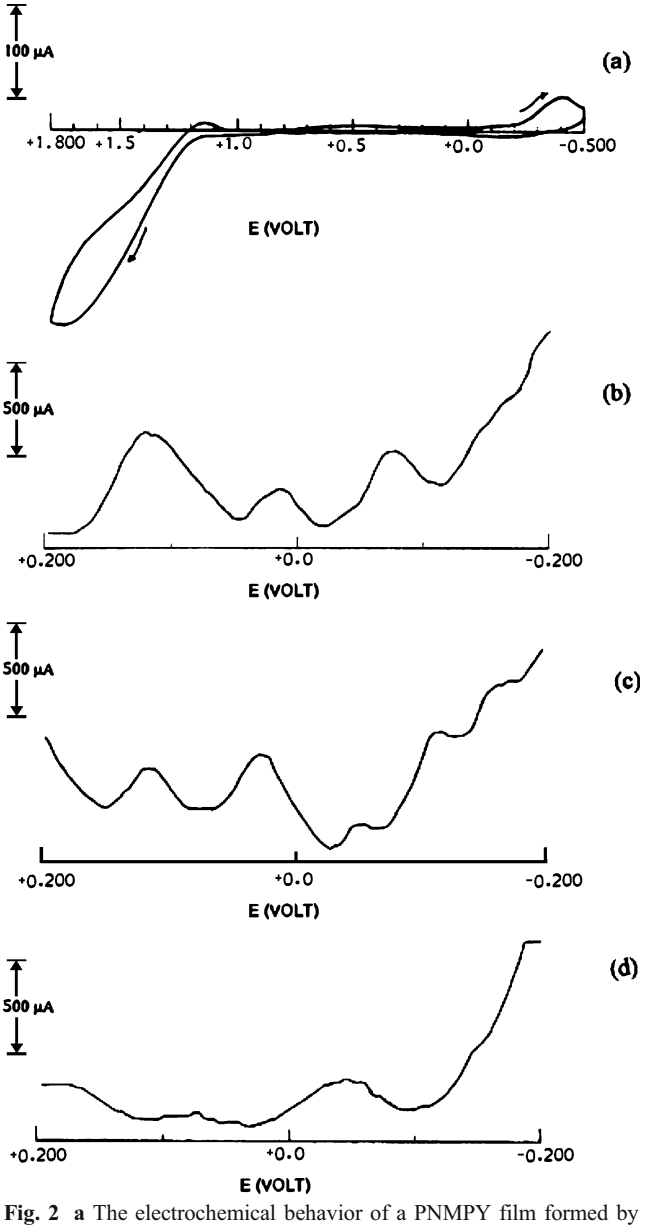

Fig. 2 **a** The electrochemical behavior of a PNMPY film formed by repeated cycles (10 cycles) in 0.1 M KCl, E_i=−0.5 V, E_f=+1.8 V, ν=50 mV/s. **b** OSWV (frequency=15 Hz, sample width=25 mV) of the PNMPY/Cu–phthalocyanine film, modified by method I, in 0.1 M KCl. **c** OSWV (frequency=15 Hz, sample width=25 mV) of the PNMPY/Cu–phthalocyanine dissolved in 0.1 M KCl. **d** OSWV (frequency=15 Hz, sample width=25 mV) of PNMPY/Cu–phthalocyanine/PNMPY film in 0.1 M KCl

(i.e., the system phthalocyanine/polymer) is ca. 100 Å as estimated from the charge passed during the electrosynthesis steps.

Electropolymerization of 3-methylthiophene and its modification with phthalocyanines

The electropolymerization of MT over a Pt surface by repeated cyclic voltammograms is shown in Fig. 3a. The current increases during both the forward and revere scans as the number of cycles increases. The results are in good agreement with those reported earlier by Tourillon and Garnier [16]. In another experiment, the Pt disk electrode was dip-coated with a CuPc as described in the first method of modification (cf. "Experimental" section) before the electropolymerization step. Cycling the potential over the electrode in the monomer-containing solution followed this step. The resulting cyclic voltammograms are given in Fig. 3b and displayed similar behavior as those observed in Fig. 3a. At this stage, the presence of a "thin" MPc layer over the Pt surface did not affect the electropolymerization mechanism of MT.

On the other hand, the effect of changing the substrate from Pt to GC proved ty affect the electropolymerization of MT. Thus, Fig. 4a,b shows the repeated cyclic voltammograms for the electropolymerization of MT at GC and GC coated with CuPc (as previously described in the case of Pt), respectively. The electropolymerization of MT over GC electrode shows similar trend as that over the Pt surface with a slight increase in current (cf. Fig. 4a). However, the application of the CuPc to the GC surface before the electropolymerization step revealed distinct behavior when compared to that at Pt surface (cf. Fig. 4b). Thus, the first cycle shows an anodic peak at ca. +1.18 V, and the reverse scan shows two cathodic peaks at +0.9 and +0.5 V, respectively. Subsequent cycles are characterized by the appearance of two anodic peaks at +1.05 and +1.22 V, respectively. And finally, the sharp peaks disappear, and the regular behavior is displayed with the appearance of rather broad peaks in the forward and backward directions. The diagram of Fig. 5 could be used to explain schematically the cyclic voltammetric response during film formation.

Modification of poly(3-methyl thiophene) (PMT) with Co–phthalocyanine effect of changing the central metal

Phthalocyanines are obtained by interaction of phthalonitrile with metal halides in which the metal ions play an essential role as templates [17]. The radius of the central hole is fixed, and it can be altered to some extent by puckering of the rings [18]. Metal fitting inside the hole of

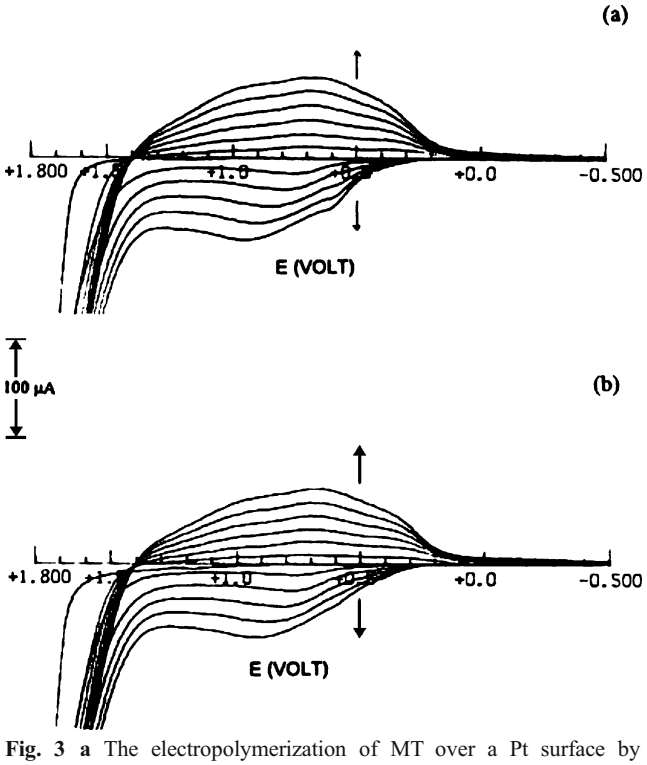

Fig. 3 **a** The electropolymerization of MT over a Pt surface by repeated CVs (five cycles), E_i=−0.5 V, E_f=+1.8 V, ν=100 mV/s (0.05 M MT, 0.05 M TBATFB/AcN). **b** The electropolymerization of MT (as in Fig. 3a) over a Pt electrode coated with Cu–phthalocyanine layer

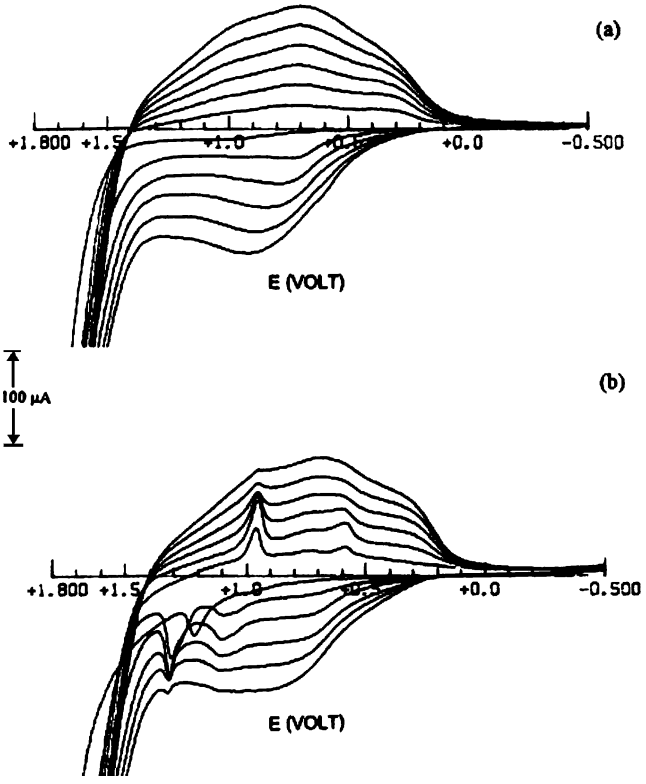

Fig. 4 **a** Repeated CVs (six cycles), E_i=−0.5 V, E_f=+1.8 V, for the electropolymerization of MT at a GC electrode, ν=100 mV/s, (0.05 M MT, 0.05 M TBATFB/AcN). **b** Same as in Fig. 4a over GC coated with Cu–phthalocyanine layer

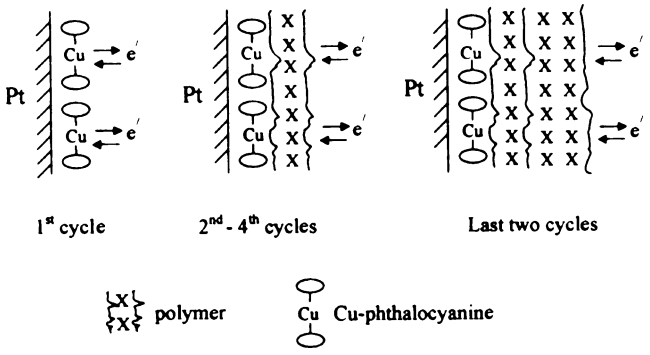

Fig. 5 Schematic diagram of the cyclic voltammetric response during film formation as in Fig. 4a,b

the phthalocyanine should therefore vary, and this will consequently affect the mechanism of the redox reaction of the complex.

CoPc layer was applied to the surface of Pt and GC according to the first method described in the "Experimental" section. The surface of the electrode was air-dried, then a PMT film was electropolymerized. In contrary to the application of CuPC layer over the electrode, the modification of the surface with CoPc displayed the same effect on the electropolymerization step of MT over both Pt and GC surfaces. Thus, the repeated cyclic voltammograms for the electropolymerization of MT on Pt and GC precoated with CoPc layer are shown in Fig. 6a,b, respectively. In both figures, the first cycle shows a distinct peak in the forward direction at ca. +0.83 V (compare this peak to that at +1.05 V in the case of growing PMT over GC coated with CuPc). Higher currents appear both in the forward and reverse directions, which indicate film thickening. However, current values are relatively higher for films formed over GC, and two peaks appear in the forward segment of the third cycle at +0.9 and +1.2 V, respectively. The schematic diagram of Fig. 5 could be used to explain the electropolymerization of MT over GC or Pt coated with CoPc layer.

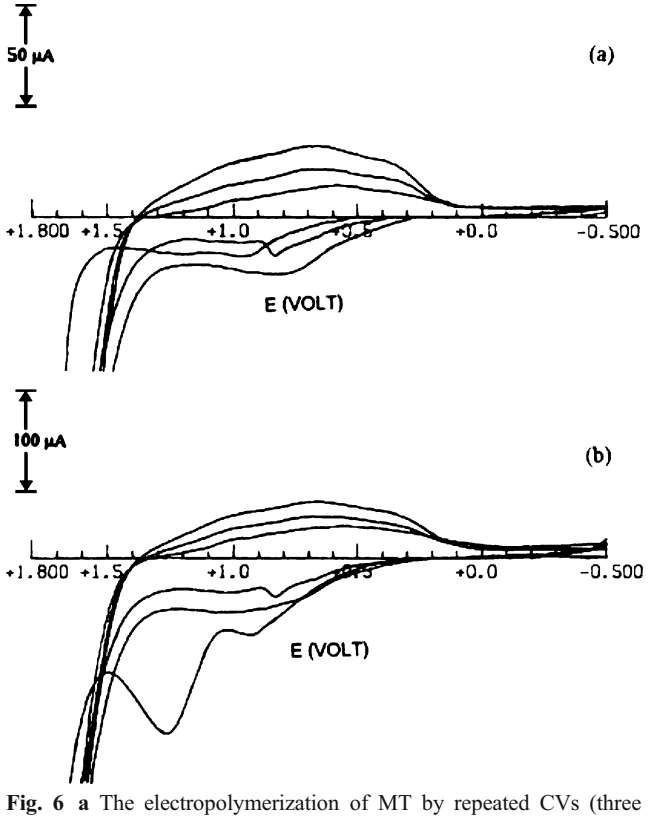

Fig. 6 **a** The electropolymerization of MT by repeated CVs (three cycles) (as in Fig. 4a) over a Pt electrode coated with Co–phthalocyanine layer. **b** The electropolymerization of MT (as in Fig. 4a) over a GC electrode with Co–phthalocyanine layer

The difference in the data obtained when using Pt surface could be attributed to the difference in Co– and Cu–Pc structures, namely, the cavity size/metal size ratio and its mode of adsorption at the electrode surface. This assumption could be ascertained by running a surface-enhanced Raman or surface reflectance FTIR spectroscopy experiments that are not available at this time.

Conducting polymer electrodes modified by sol–gel layers containing phthalocyanine

The sol–gel layers were prepared by silicate hydrolysis and condensation to form poly(silicates). If we consider the first step as the hydrolysis of an ester, in this case, tetraethoxy silicate in an acid medium would be:

$$Si(OEt)_4 + H_2O\ (excess) \rightarrow Si(OH)_4 + 4EtOOH$$

In this work, alcohol was used as the hydrolyzing agent. The formed silicic acid slowly thickened in solution and finally gelled. In addition, according to Iler [19], silicic acid polymerizes into discrete particles that in turn aggregate into chains and networks. The polymerization of the monomer leads to the formation of particles. Consequently, particles grow, and finally, gel is formed as a result of the network established. The extent of gelation can be noticed in terms of the increase in the viscosity of the medium. Particles are formed with dimensions ranging between 30 and 100 nm [19]. The corresponding MPc was added before the mixing of alcohol and before the polycondensation process started. The MPc contained in the gel was applied to the electrode by dip coating. The film was then dried and immediately characterized. On a microscopic level, this silica surface is composed of open and closed rings of various sizes [20]. Two important consequences result from this structure: (1) surface hydroxyl groups on the surface are sites where physical adsorption of water, and other polar molecules, occurs, and (2) the porosity of the surface allows the interactions of the Pc in the silicate with the electrolyte.

The modification of the conducting polymer was performed according to the following scheme: PMT was

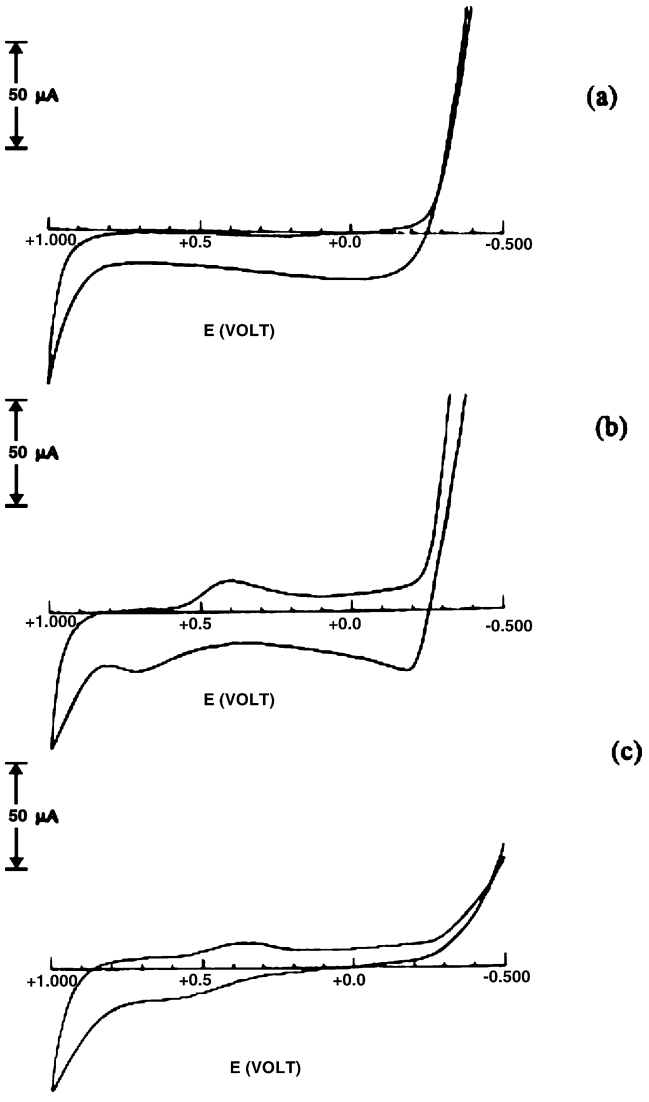

Fig. 7 **a** CV of PMT over Pt electrode in 0.1 M H_2SO_4, E_i=−0.5 V, E_f=+1.0 V, ν=50 mV/s. **b** CV of PMT grown on Pt electrode and covered with Cu–phthalocyanine sol–gel in 0.1 M H_2SO_4, E_i=−0.5 V, E_f=+1.0 V, ν=50 mV/s. **c** CV of PMT grown on Pt electrode and covered with Co–phthalocyanine sol–gel in 0.1 M H_2SO_4, E_i=−0.5 V, E_f=+1.0 V, ν=50 mV/s

electrodeposited over Pt or GC using repeated cycling as described before. The resulting polymer was thoroughly rinsed with AcN, dried, and then dip coated with the Cu– or Co–PC/sol–gel. Cyclic voltammograms of Pt/polymer, Pt/polymer/sol–gel (CuPc), and Pt/polymer/sol–gel (CoPc) in 0.1 M H_2SO_4 are shown in Fig. 7a–c, respectively. The following observations could be made: (1) high currents are displayed in the hydrogen evolution region, i.e., at potentials less than −0.25 V for Pt/polymer and Pt/polymer/sol–gel (CuPc) electrodes, (2) relatively large peak is observed for hydrogen gas with the second electrode only, (3) two quasi-reversible peaks at +0.68 V (forward scan) and +0.40 V (reverse scan) are observed for the second and third electrodes, and (4) for the three electrodes, high currents start to develop with the onset of oxygen evolution. The foregoing data indicate that charge transfer takes place at the Cu– and Co–Pc-modified sol–gel polymer electrodes. Slow charge transfer is expected in this case depending on the diffusion of the ionic species through the sol–gel pores and the availability of the MPc moieties to reach the sol–gel electrolyte interface. It is established that film-modified electrodes are designed to facilitate the electrode process [21]. For these hybrid films, we may consider a Pt or GC substrate, covered with a conductive polymer layer, and a sol–gel layer containing the Cu– or Co–Pc. Charge transfer takes place within the sol–gel layer from an MPc center to another and is controlled mainly by diffusion. Two heterogeneous charge transfer processes take place, the first at the sol–gel/electrolyte interface and the second transfer also takes place at the sol–gel/polymer interface. Moreover, MPc moieties can migrate through the sol–gel layer that depends on several factors including film morphology and solvent penetration. According to Bard and Faulkner [21], an apparent diffusion coefficient D_{ct} can be defined as a contribution from the physical movement of the electroactive species and the electron transfer process:

$$D_{ct} = D + k\delta^2 C^b \quad (1)$$

where δ is the distance between sites for electron transfer, b is a numerical constant (frequently taken as $\pi/4$ or 1/6 for three-dimensional diffusion [21], C is the total concentration of active sites, k is the rate constant, and D is the translational diffusion coefficient.

The effect of changing the solid electrode from Pt to GC on the electrochemical response of the substrate/polymer/sol–gel(MPc) system was also studied. As was discussed in the previous section, the solid electrode on which the polymer was electrochemically grown plays a key role in the electrochemical response after its modification with the MPc layer. Figure 8a,b shows the cyclic voltammetry response of PMT films grown on GC and modified with a sol–gel layer containing CoPc. The method of preparing the "bilayer" electrode is as described in the previous section. Figure 8a compares the cyclic voltammogram of PMT/GC (I) and GC/PMT/sol–gel (II) films in 0.1 M H_2SO_4. Each cyclic voltammogram is characterized by a distinct peak that appeared at +1.6 and +1.4 V for systems I and II, respectively. An explanation that justifies this difference is the availability of anionic species at the film/electrolyte interface. It is clear that the doping process for system II electrode is thermodynamically more favored compared to system I electrode. This is evident when comparing the anodic peak potentials of the voltammograms of Fig. 8a. On the other hand, the relatively lower peak current observed for the polymer modified with the sol–gel is due to the relatively high resistance of the silicate within the film. The inclusion of the CoPc within the sol–gel matrix

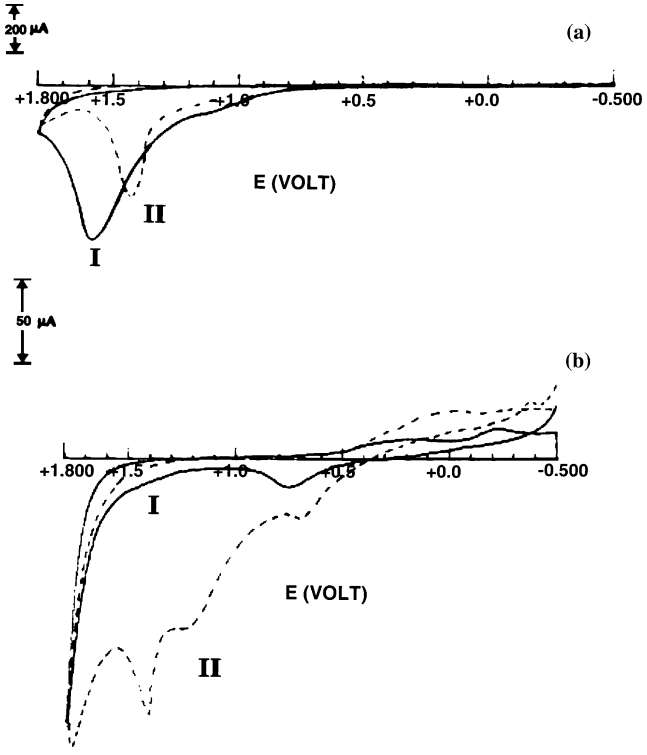

Fig. 8 **a** CV of PMT on GC electrode I (—) and on GC electrode modified with sol–gel layer II (---) containing Co–phthalocyanine in 0.1 M H_2SO_4. E_i=−0.5 V, E_f=+1.8 V, ν=50 mV/s. **b** CV of GC electrode modified with sol–gel layer containing Co–phthalocyanine I (—) and of PMT film grown on GC and covered with sol–gel layer containing Co–phthalocyanine II (---) in 0.1 M H_2SO_4. E_i=−0.5 V, E_f=+1.8 V, ν=50 mV/s

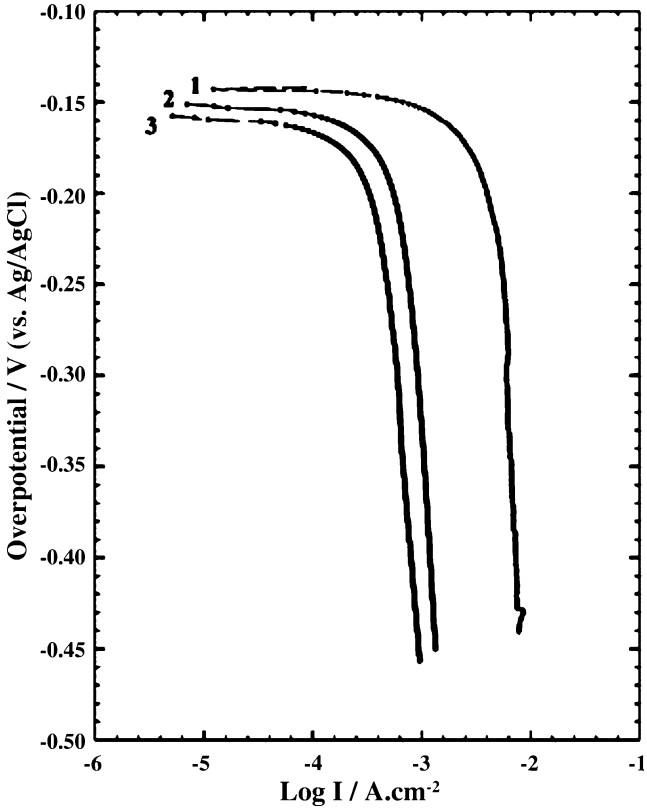

Fig. 9 Tafel plots for PMT-coated Cu-phthalocyanine (1), PMT (2), and Pt-coated Cu-phthalocyanine (3), in 1 M H_2O_2/2 M KOH

gave interesting results. Thus, the cyclic voltammograms of Fig. 8b show the electrochemical behavior of GC/sol–gel (CoPc) (system I) and GC/PMT/sol–gel (CoPc) (system II). Several observations and conclusions can be withdrawn: (1) the redox behavior of the cobalt is noticed with an anodic peak appearing at +0.75 V (system I) and +0.70 V (system II) and a cathodic peak at −0.2 V (system I) and +0.1 V (system II), (2) in the case of system II, a shoulder at +1.25 V preceding a distinct anodic peak at +1.4 V, and (3) current values are generally high for the entire potential window for system II. The presence of cobalt–phthalocyanine within the sol–gel matrix mediates the doping process of the underlying polymer layer, which results in lower peak potential and larger current values (ca. electrochemical response of system II in Fig. 8a). Moreover, larger current values are observed for potential values higher than +1.7 V. Mediated charge transfer is expected by the Co-containing moieties according to the aforementioned charge mediation explanation. Again, restricted diffusion of the mediator is expected that results in the anodic shoulder.

The increase in the thickness of the sol–gel layer containing the MPc was also studied (data not shown). In this respect, higher current values are obtained for potential values less than 0.0 V and higher than +1.2 V for the thicker film. Also, a couple of redox peaks appear at +0.52 and +0.3 V in the forward and reverse scans, respectively. This is explained by the fact that the increase in the sol–gel containing MPc results in the enrichment of the number of active sites responsible for current amplification. Since the metal–phthalocyanine moieties take part in the electrochemical charge transfer process, when the time elapsed for dip coating the phthalocyanine layer was doubled, the current signal measured at the quasi-redox peaks increased by 62%.

Phthalocyanine-modified conducting polymer films for the hydrogen peroxide electrocatalysis

Hydrogen peroxide is a rational choice as an oxidant used in storage tanks for fuel cells when air is in short supply [22]. Hydrogen peroxide possesses several features that make it the appropriate candidate for such application, namely, nontoxicity, storability, and high specific energy. On the other hand, noble metals such as Pt, Pd, or Au are usually used as oxygen electrocatalyst [23]. However, hydrogen peroxide heterogeneously decomposes to oxygen at these surfaces, which results in propellant waste, and side

nondesired reactions take place such as surface desorbed hydroxide radicals [24]. Therefore, the use of catalytic surface that does not result in heterogeneous decomposition will be advantageous.

In basic solution, the overall reaction for the hydrogen peroxide reaction can be written as:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$$

Gibbs free energies of the molecules allow the estimation of the standard reversible potential of this process to be +0.88 V. This value is both pH and H_2O_2 dependent. On the other hand, when using a Pt surface, the value reduces to 0.0 V [25].

For a given chemical reaction, the rate of reaction and the temperature are related by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{2}$$

where E_a is the activation energy, and other terms assume normal meanings. In the present case, the modification of the surface results in a catalyzed reaction, and the rate of reaction increases. Thus, for the electrochemical reaction that takes place at the electrode surface, the current density (i) and the standard overpotential (η) are related according to [26]:

$$i = ce^{\left(\frac{-E_a + B(E^\circ - \eta)}{RT}\right)} \tag{3}$$

In this equation, c is equivalent to $nFk_a[M^{n+}]$, and B is equivalent to $(1-\alpha)nF$. While the application of "sufficient" overpotential should result in an increase of reaction rate, however, it is desirable to decrease the activation energy while applying low overpotentials (ca. 50 to 300 mV) to the "working" electrode. The relation between (η) and the current density (i) is given by:

$$\eta = a + b \log i \tag{4}$$

Using a first-order approximation, the constants a and b can be derived as:

$$a = 2.3\frac{RT}{\alpha F}\log i_o \tag{5a}$$

$$b = -2.3\frac{RT}{\alpha F} \tag{5b}$$

The values of a, b, i_o, and the charge transfer coefficient α can be found from a linear least-squares fit of the Tafel experiments. The value of α depends on the electrochemical conditions including the type of reactants at the electrode surface. The value of α was found to be in the order of 0.2 [27] compared to 0.5 that is expected for most electrochemical reactions. The exchange current density, i_o, will be taken here as a measure of the extent of the electrocatalysis. A typical Tafel plot with curve fits is shown in Fig. 9.

The relationship of Eq. (4) fails at low overpotentials because it assumes that the reaction proceeds in one direction and that reversibility is less likely. When the "applied" overpotential is very small, both forward and reverse reactions are likely. In this case, the current values are much smaller than predicted. On the other hand, at high overpotentials, the reaction proceeds under diffusion-controlled conditions, and the above relationship fails again. The electrode surface is also expected to remain "stable" throughout the course of measurement.

Recently, several surfaces have been tested for the electrocatalysis in hydrogen peroxide fuel cells [28–30]. Among those tested, titanium is known to corrode [29], and the electron transfer is known to be much slower on others such as nickel compared to Pt [30]. Tafel plots should give an indication of the extent of reaction at these surfaces and for the presently studied films. The linearity of the Tafel region and its extent will be a function of the adsorption/desorption mechanism for the reduction process. Typical plots of the overpotential η vs log i as given in Eq. (4) for Pt-coated Cu–phthalocyanine, PMT, and PMT-coated CuPc are shown in Fig. 9. The curves displayed in Fig. 9 show that the three surfaces have electrocatalytic potentials for the reduction of hydrogen peroxide. The rest potentials for these electrodes are −0.160, −0.150, and −0.120 V, respectively. These values reflect the adsorption/deposition processes of the hydroxyl groups. For the PMT-coated CuPc, the Tafel plot shows a slight change in the slope at ca. −300 mV. This is possibly due to a change in the reaction mechanism as the potential decreases. On the other hand, in the high-current region, the exchange current density for the CuPc-modified PMT is relatively higher when compared to the two other surfaces (cf. Table 1). All three electrodes show evolution of gas when the current passing is almost zero. The relatively high current of CuPc-modified PMT suggests their use as a fuel cell electrode material. The long-term stability of these surfaces was not tested. Also, a more complete study of other metal–phthalocyanine for their use as electrode materials with different fuel cells is recommended. The performance of the

Table 1 Rest potentials and exchange current densities for different films tested for the electrocatalysis of hydrogen peroxide reduction

Electrode surface	Rest potential vs Ag/AgCl, (V)	Exchange current density (A cm^{-2})
Pt/Cu–phthalocyanine	−0.160	3.89×10^{-4}
PMT	−0.150	6.78×10^{-4}
PMT/Cu–phthalocyanine	−0.140	2.31×10^{-3}

modified conducting polymer surface and its efficiency for hydrogen peroxide reduction are reasonably accepted when compared to other surfaces such as zinc and gold [31], and iron tetramethoxy phenyl porphyrin and lead sulfate electrodes [32].

Conclusion

We have investigated the inclusion of complexes such as Cu– and Co–pthalocyanines into conducting polymer matrices of PMT. The electrochemical behavior of the resulting "hybrid" films depends on the method of application of the complex to the polymer structure. The following electrode configurations were studied: phthalocyanine and (Pt or GC)/phthalocyanine/polymer. In all cases, the charge transfer due to the presence of phthalocyanine was displayed, and the substitution by Co for Cu in the phthalocyanine moiety proved that changing the type of substrate from Pt to GC does not affect the electrochemical behavior of the phthalocyanine-modified polymer electrode in the case of Co when compared to Cu. The kinetics of charge transfer at the hybrid film/electrolyte interface was controlled by diffusion in the case of sol–gel modification. The sol–gel-modified conducting polymer film was applied successfully for the reduction of hydrogen peroxide. Moreover, the amount of current passing in the hydrogen evolution region was relatively high compared to the unmodified films.

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