

**Adsorbed Monomeric and Electropolymerized Cobalt Tetra-Amino Phthalocyanine Modified Electrodes : Effect of Film Thickness on the Electro-Oxidation of 2-Mercaptoethanol.**

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Unsubstituted and substituted transition-metal phthalocyanines adsorbed on graphite electrodes at monolayer levels exhibit substantial electrocatalytic activity for the oxidation of several thiols like cysteine, glutathione and 2-mercaptoethanol (1,2). However, these electrodes are not stable over long periods of time. Only few examples have been reported to attempt to develop the use of polymer-based phthalocyanine films for the activation of thiols, to offer a better alternative to the design of efficient and stable electrocatalysts (3,4). An analysis of comparative studies reporting on this point has shown that much advantage can be obtained by employing macrocyclic complexes with functional groups on the periphery of the ligand that can be electrochemically polymerizable upon oxidation (4,5).

In this context, we explore here the electrocatalytic activity of adsorbed monomeric cobalt tetra-aminophthalocyanine, CoTAPc, and of electropolymerized poly-CoTAPc films for the oxidation of 2-mercaptoethanol. We report, for the first time, a comparative study of the electrocatalytic behaviour of these chemically modified electrodes as a function of CoTAPc film thickness.

Figure 1 illustrates the response of a poly-CoTAPc film, prepared by 24 electropolymerizing scans on vitreous carbon electrode, after adding 1 mM of 2-mercaptoethanol (2-ME) to the electrolytic 0.5M NaOH solution. In these conditions, a large oxidation current is observed as soon as -0.45 V/sce, which is related to the electrocatalytic oxidation of 2-ME. The apparition of the oxidation peak at  $E_{pa} = -0.29$  V/sce is concomitant with that of a reduction peak at -0.86 V/sce, during the reverse scan, which may be related to the reduction of the corresponding disulphide.

Table 1 illustrates the effect of film thickness on the electrocatalytic properties of poly-CoTAPc. The data relative to the adsorbed layer of CoTAPc are also reported. The first remark that should be emphasised here is that the most active electrode, in terms of current intensity, peak potential and apparent rate constant  $k$  for 2-ME oxidation process, is that modified with an adsorbed layer of CoTAPc. The second important remark is that the activity of electropolymerized films improves with its thickness, but very slightly. However the improvement of the catalysis for the reduction of the disulphide is more pronounced, using the same criterion. The difference in activities is more dramatic between the adsorbed CoTAPc and the poly-CoTAPc film prepared with 2 electropolymerizing scans. It appears from these results that the totality of the cobalt centres imbedded inside the films of poly-CoTAPc are not electroactive, as previously suggested (5). Only few external layers located on the film/solution interface are electrocatalytically active towards 2-ME oxidation. Indeed, there is no substantial increase in the faradaic currents by increasing the film thickness. Thus, there is no intervention from CoTAPc located in the bulk of the film: the adsorbed monomeric CoTAPc still be the most active one.

Finally, an analysis of the stability of the examined adsorbed and electropolymerized catalyst modified electrodes showed that even though monomeric CoTAPc adsorbed on glassy carbon presents higher activity for the electro-oxidation of 2-ME, the high stability of the electropolymerized poly-CoTAPc makes them more attractive for applications in the activation and/or the amperometric detection of thiols.

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Fig.1. Cyclic voltammograms of electropolymerized poly-CoTAPc film in 0.5 M NaOH aqueous without (curve a) and with (curve b) 2-ME (1 mM) ( $\nu = 0.2$  V/s)

Table 1. Electrocatalytic characteristics of CoTAPc films towards the oxidation of 2-ME (1 mM) in 0.5M NaOH solution.

CoTAPc film thickness	$E_p^a$ (V/sce)	$I_p^a$ ( $\mu$ A)	$E_p^c$ (V/sce)	$10^4k$ (cm/s)
Adsorbed ( $\approx 0.5$ nm)	-0.32	23.2	-0.80	20
Polymer $\approx 5$ nm	-0.28	21.1	-0.90	1.7
Polymer $\approx 60$ nm	-0.29	21.6	-0.86	5.8
Polymer $\approx 200$ nm	-0.30	22.5	-0.83	12.1

(a) potential oxidation peak, (b) current intensity; (c) disulphide reduction potential (measured by cyclic voltammetry at 0.2 V/s).  $k$  = rate constant of 2-ME oxidation (at -0.4 V/sce).

