

Emphasis on the Effects of Adsorbed Cobalt Phthalocyanine Surface Concentrations on the Electrocatalysis of 2-Mercaptoethanesulfonic Acid Oxidation.

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The detection of thiol-derived substances is an important field of research as they can be present as contaminants in fuels and biological fluids. During the last decade, it has been reported that electrodes modified by adsorbed transition metal phthalocyanines show substantial electrocatalytic activity for the electro-oxidation of thiols [1]. Only few examples have been reported to attempt to develop the use of multilayered-based metallophthalocyanine films for the activation of thiols, to offer a better alternative to the design of efficient and stable electrocatalysts [2-4]. In this context, in a recent work we explored the electrocatalytic activity of electropolymerized cobalt tetraaminophthalocyanine (CoTAPc) films for the oxidation of 2-mercaptoethanol [5] and reported, for the first time, a comparative study of these chemically modified electrodes as a function of CoTAPc film thickness.

In this report, we extend our investigations to the activation of a new thiol derivative target, namely 2-mercaptoethanesulfonic acid (2-MESA). We describe here the electrocatalytic oxidation of 2-MESA at graphite electrodes modified with adsorbed cobalt phthalocyanine CoPc and electropolymerized CoTAPc.

In the case of adsorbed CoPc, analysis of the cyclic voltammograms of modified OPG electrodes obtained with different contact times with the catalyst solution clearly shows that the apparent electroactive sites are ranging from of 5.6×10^{-11} to 106.6×10^{-11} mol/cm², depending on the contact time used for the preparation of the modified electrode.

Fig. 1 (curve 2) illustrates the response of an OPG electrode modified with 10.6×10^{-11} mol/cm² of CoPc adsorbed on its surface, after adding 0.5 mmol.L⁻¹ of 2-MESA to the electrolytic 0.1 mol.L⁻¹NaOH solution. Under these conditions, a large oxidation current is observed at potentials as low as -0.25 V, which is related to the electrocatalytic oxidation of 2-MESA at the modified electrode. Fig. 1 also illustrates the effect of the deposited amount of CoPc on the electrocatalytic oxidation of 2-MESA (curve 1). Indeed, besides the increase of the oxidation peak current with the electrode surface concentration, it appears that for amounts of adsorbed CoPc lower than 15.2×10^{-11} mol/cm², the cyclic voltammograms show a single oxidation peak which gradually shifts to more negative values as the electrode coverage increases, while those obtained with higher amounts of adsorbed CoPc exhibit two peaks. This clearly shows that 2-MESA oxidation process occurs, for submonolayer CoPc surface concentrations, in a different way than at OPG electrodes modified with higher surface concentrations that correspond to the formation of adsorbed CoPc multilayers (6 to 9 equivalent monolayers).

In order to understand the multilayer effects on the thiol electro-oxidation process, experiments were performed with the electropolymerizable CoTAPc catalyst. By comparing the behaviour of CoPc with that of CoTAPc modified electrodes, it appeared that (i) for 1 equivalent monolayer coverage, both adsorbed CoPc and CoTAPc behave similarly (the oxidation of 2-MESA occurs through one single peak that appears at ca. -0.2 V) and (ii) the cyclic voltammogram of the thick electropolymerized poly-CoTAPc in presence of 2-MESA exhibits 2 peaks, similarly to that of multilayered adsorbed CoPc modified electrode. The remarkable result is that for the CoTAPc complex, the splitting of the 2-MESA electrocatalytic oxidation peak occurs for the polymer coating, although the apparent surface concentration is rather similar to that of the adsorbed CoTAPc modified electrode.

Analysis of our results shows that the electrocatalytic oxidation of 2-MESA at cobalt phthalocyanine modified electrodes is sensitive to the surface concentration of the catalyst, suggesting the formation of "sandwich" like structures involving two adsorbed CoPc molecules bound to one 2-MESA, for low CoPc surface concentrations, while such a situation does not occur for more tightly packed complex multilayers. Nevertheless, for both adsorbed and electropolymerized multilayered coatings, a splitting in the oxidation peak of 2-MESA was observed. This unique behavior, typical of 2-MESA, may be rationalized by the different acidity, ligation and hardness properties of the 2-MESA ending groups, SO₃⁻ and S⁻, contrarily to S⁻ and O⁻ present in the parent 2-mercaptoethanol. Investigations are under progress in order to evaluate these observation in terms of molecular orbital theoretical calculations.

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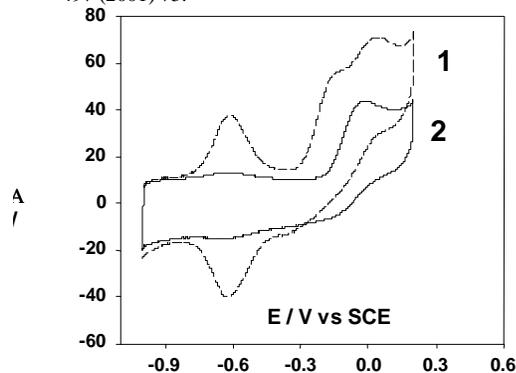


Fig.1. Cyclic voltammograms of an OPG electrode modified with 10.6×10^{-11} mol/cm² (curve 1) and 106.6×10^{-11} mol/cm² (curve 2) of CoPc adsorbed on the surface after adding 0.5 mM 2-MESA to 0.1 M NaOH aqueous solution purged with N₂. Scan rate: 0.1 Vs⁻¹.