

“Characterization of Poly-Tetraaminophthalocyanine-Modified Electrodes. Electrocatalytic Reduction of Molecular Oxygen”

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In the last decade, a new kind of conducting polymer has been developed (1). The units or “monomers” are transition complexes with macrocyclic ligands, which permit the electronic conductivity. Generally, the complex has a geometry predominantly planar, in order to favor the interactions between the π cloud and the electrodic surface. These complexes need to have oxidizable substituent groups in the periphery of the ring to permit the electropolymerization.

In our previous work (2,3), we have investigated the electrocatalytic behaviour of poly-metal-tetraaminophthalocyanines, and in these cases, we also have found a little activity of the polymerized ligand. However, the activity of the polymerized ligand strongly depends on the conditions of electropolymerization. For that reason, in this work we have prepared the free base, with different solvents and potential limits, poly-tetraaminophthalocyanine (H₂PcTA)- modified electrodes in order to compare the different modified electrodes as electrocatalysts for the reduction of molecular oxygen.

The structure of a H₂PcTA ligand has four amino groups that can be located in different positions of the terminal benzenes of the ring. These amino groups are the responsible of the electropolymerization of the molecule, due to its irreversible anodic oxidation.

The macrocyclic ligand, H₂PcTA, was electropolymerized on a glassy carbon electrode by continuously potentiodynamic scans, using two different solvents, dimethylsulfoxide (DMSO) and dimethylformamide (DMF). The electrosynthesis of the polymer (p-H₂PcTA/DMSO and p-H₂PcTA/DMF) was performed by continuously cycling the electrode potential between -0.6 and +1.15 V (large limits of potential) or -0.6 and +0.9 V (short limits of potential) versus Ag/AgCl, at 200 mVs⁻¹, for 20 or 100 potentiodynamic cycles.

The voltammetric responses in aqueous-N₂-bubbled solution at pH 13 of the polymers grown in DMSO or DMF are very different. The p-H₂PcTA/DMSO shows an ill-defined voltammogram except when it was electrosynthesized with 20 cycles. In this case, its voltammetric response shows a reversible couple at ca. -0.6 V. On the other hand, data obtained with EIS show that the polymer obtained in DMSO (large limits) is very thin compared to that obtained in DMF (under similar conditions). It can be attributed to an over-oxidation process that takes place in DMSO, due to its higher σ donor capacity, which causes a decreasing in charge at the end of the electropolymerization. Both polymers are more conductive in the presence of O₂ than in N₂.

The voltammetric responses of all the polymers for the reduction of molecular O₂ are also different (see Figure 1). The reduction current is higher in DMF than the currents obtained with p-H₂PcTA/DMSO, but it is due to the higher charge of the polymer grown in DMF. All the

polymers show a unique reduction wave except the polymer grown in DMSO with only 20 cycles, which depicts two reduction waves. The first reduction peak (at more positive potentials) appears in the same potential for the polymer grown in DMF and the polymers obtained in DMSO with short limits or 20 cycles (at ca. -0.3 V). This peak appears at more negative potential for the 100 cycles polymer grown in DMSO, with large limits (at ca. -0.5 V). On the other hand, as mentioned above, only one system shows a second process for the reduction of molecular O₂ in the potential limits studied. That is the case of 20 cycles polymer, grown in DMSO. Then, the best catalyst is the polymer grown in DMSO with 20 cycles of potentiodynamic scans. The fairly modified electrode is that obtained in DMSO with 100 cycles and a positive potential limit of +1.15 V. It depicts only one cathode signal at very negative potentials. As mentioned above, in this case, during the electropolymerization, an over-oxidation process takes place, which partially destroy the film and inhibits its electrocatalytic activity for the reduction of O₂ compared to the polymer grown in DMF. To avoid this over-oxidation, two posibles ways can be used. To achieve the electropolymerization during a lower number of potentiodynamic scan or using a positive potential limit shifted to more negative potential.

References

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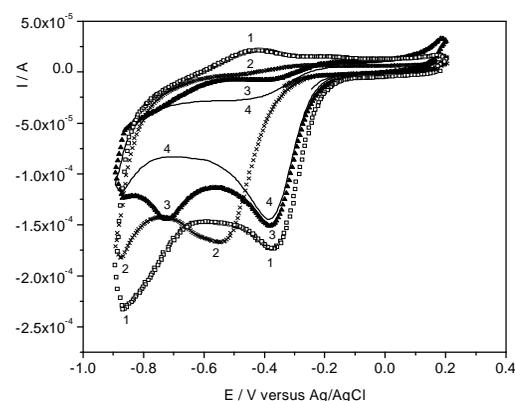


Figure 1. Voltammetric response in aqueous oxygenated solution at pH 13 of

- 1: p-H₂PcTA/DMF (100 cycles, large limits of potential)
- 2: p-H₂PcTA/DMSO(100 cycles, large limits of potential)
- 3: p-H₂PcTA/DMSO (20 cycles, large limits of potential)
- 4: p-H₂PcTA/DMSO(100 cycles, short limits of potential)