ANALYSIS BY SCANNING ELECTROCHEMICAL MICROSCOPY OF ELECTROACTIVE SURFACES AND DEVELOPMENT-CHARACTERIZATION OF TEXTILE FIBER CARBON ELECTRODES

An important part of the work carried out in the present thesis is based on the developement and application of the scanning electrochemical microscopy (SECM). By means of this technique, surfaces coated with different electroactive materials developed by our research group, were analyzed. The electroactive materials are synthesized on different substrates in order to get working electrodes for the electrochemical treatment of wastewater polluted with azo dyes from dyeing processes in textile industries. Among the modified surfaces with electroactive materials are included:

- Dimensionally stable anodes (DSAs) prepared from a Ti surface coated with SnO_2 (Ti/SnO_2), Sb-doped (Ti/ SnO_2-Sb) and Pt-stabilized (Ti/ SnO_2-Sb-Pt).
- Polyester fabric (PES) coated with polypirrol (PES/PPy) and doped with anthraquinone sulfonate (PES/PPy-AQSA) or phosfotungstate (PES/PPy-$PW_{12}O_{40}^{3-}$).
- PES textile coated with polyaniline (PES/PANI) synthesized in sulphuric (PES/PANI-HSO_4^-) and chlorhidric (PES/PANI-Cl^-) acid solutions.
- Thread of Pt coated with PANI and electrodispersed Pt (Pt/PANI-Pt).
- Activated carbon fiber textile coated with PANI (C/PANI) and or without electrodispersed Pt (C/PANI-Pt).
- PES textile coated with graphene oxide (GO) and its reduced form (RGO).

Local analyses carried out on these surfaces allowed us to determine their electroactivity in relation to $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ redox couples selected as mediators.

Experimental approach curves, obtained in *feedback* mode, were compared to the theoretical ones in accordance with SECM theory for a conducting substrate (*feedback* +) or an isolating substrate (*feedback* -). By means of 2D and 3D SECM images was possible to observe the distribution of the electrochemical activity in the different samples. The results allowed us to validate the synthesis processes in accordance with their electroactivity and the homogeneous distribution. A notable aspect was the influence on the SECM images of the topography of the textile substrate. In this case, the superficial electroactivity reproduces the geometrical pattern of the fabric.

The influence on the electrochemical activity of aspects such as: life time /corrosion for DSAs, kind of dopant/pH for PES/PPy samples, influence of pH for PES/PANI samples, oxidation state of the electroactive material and the influence of the mediator (redox couple) for graphene, has been clearly noticed in SECM studies.

A second important part of the work developed in this thesis, appears as a continuation of the researches that are being carried out by our research group. Thus, in chapter 2 of the present thesis is studied the development, characterization and application of electrodes made from activated carbon fiber fabric. The objective of the development of these electrodes is based on their applications to industrial processes such as: electrooxidation of relatively simple molecules type methanol or, in accordance with our line of research, for the electrochemical treatment of water polluted with azo dyes from textile industry dyeing processes. Among the carbon fabrics developed in chapter 2, are included:

- Unmodified carbon textile electrodes.
- Carbon textile electrode modified with dispersed Pt.
- Carbon textile electrodes coated with PPy or PANI.
- Carbon textile electrodes coated with PPy or PANI with dispersed Pt.

Two geometries were chosen to develop the carbon fiber electrodes. The one-dimension electrodes (WE1D) were prepared from a yarn taken out from the fabric. The two-dimension electrodes (WE2D) were made from a band (1 cm x 3 cm) cut form the carbon fabric.

By means of cyclic voltammetry (CV) and using the WE1D electrodes, the synthesis conditions for the modified WE2D electrodes were established. The electrochemical behavior of the WE1Ds was studied by using the CV in different electrochemical systems such as: H_2SO_4, CH_3OH/H_2SO_4 and amaranth/H_2SO_4 solutions. For this last system, a glassy carbon electrode (GCE) was also used. The reason for this election was to obtain more accurate voltammetric information of the amaranth oxidation/reduction processes than with WE1D electrodes.

In the electrochemical characterization of WE2Ds, SECM microscopy played an important role. It was not possible to obtain proper voltammetric information of the synthesis processes for WE2D electrodes. Thus, SECM results allowed us to validate the synthesis conditions, some of them previously established for WE1D. In this sense, SECM appears as an alternative to CV for the measurement of the surface electroactivity and the distribution of the electrocatalytic material for these kinds of samples.

On the other hand, micrographs and stereoscopic images from the different electrodes were taken by the scanning electronic microscopy (SEM) and the stereoscopic microscope.

The voltammetric study carried out with amaranth/H_2SO_4 with the textile electrodes WE1D and GCE allowed us to choose the working potentials for the oxidation/reduction electrolysis carried out with the non modified WE2D and WE2D/Pt, WE2D/PANI-Pt modified electrodes.

With the WE2Ds electrodes different electroreductions/electrooxidations were carried out for the amaranth solution in sulphuric medium in an “H” shaped cell with separated compartments. The amaranth degradation process, what it is to say, the decolorization of the amaranth solution, was studied by means of high performance liquid chromatography (HPLC) and UV-visible, fluorescence emission and Fourier transform infrared with attenuated total reflection (FTIR-ATR) spectroscopies.

The charge efficiency of the electrolysis confirms the choice of potentials. The percentage of color removal obtained for both electroreduction and the electrooxidation processes was above 90%. It was also found that the presence of dispersed platinum brought a significant time of electrolysis reduction for the electrooxidation at 900 mV.

On the other hand, UV region, fluorescence emission and FTIR-ATR spectra allowed us to observe the differences concerning the type of processes (electroreduction/electrooxidation), type of electrode (unmodified/modified electrodes) and presence/absence of chlorides in the reaction medium. With this study, it was established a work methodology for future researches with others azo dyes, using electrodes based on the carbon fiber fabric.