PhD Thesis

Composite electrode materials based on conducting polymers

- *Summary* –

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INTRODUCTION

The research made in this PhD thesis fits the current trend in the development of new advanced composite electrode materials with high performance and parameters. The composite materials has new physical and chemical properties that are not present in its components taken individually.

The new electrode materials were obtained by combination of conducting polymers, such as polypyrrole and/or functionalized polypyrrole with inorganic materials like zeolites or carbon nanotubes and the study presents fundamental interest of new physical processes and phenomena induced by the nanostructuring of conducting polymers, interface effects, specific interactions between components, and application for a variety of interest areas: actuators, electronic devices, chemical sensors, biosensors.

The main objective of this Phd thesis is obtaining new modified electrodes architectures, using as substrate arts materials such as polymers like polypyrrole and functionalized polypyrrole and development of new composite electrode material using inorganic modification agents such as zeolites or carbon nanotubes. Complex physical and chemical characterization of the as obtained electrode materials, allowed a better understanding of the properties of this materials, offering a wide perspective of applications in various fields, especially in bioelectroanalytical chemistry.

In the first part of this work, a bibliographic study of the modified electrodes area was made, using as substrate simple or composite polymeric materials and modified inorganic agents, such as zeolites and carbon nanotubes.

The second part, the original contributions are divided into three chapters, describing the synthesis and characterization of modified electrodes:

(i) Micro and nanostructured polymeric electrode materials based on polypyrrole. In this chapterare are described the preparation methods of new modified electrode based on polymeric materials using simple or functionalized layers of polypyrrole. After obtaining these new materials, physical and chemical characterization was performed using modern techniques such FTIR spectroscopy, scanning and tunneling electron microscopy. Also, the as prepared materials were characterized in electrical, electrochemical and catalytic terms.

(ii) Polymeric composite electrode materials based on polypyrrole
In order to improve the electrochemical characteristics of modified electrodes, in this chapter were prepared new composite electrode materials, by associating of organic conducting polymeric layers such as micro and nanostructures polypyrrole with inorganic nanostructures like zeolites and carbon nanotubes. The as prepared materials were characterized in physical and chemical terms.

(iii) Composite electrode materials based on carbon paste
In this chapter were obtained new modified electrode using common materials such as carbon paste in combination with inorganic micro and nanostructures such zeolites and carbon nanotubes. The as prepared modified electrodes were characterized in physical, chemical electrochemical and catalytic terms.

PART ONE - BIBLIOGRAPHIC INFORMATION

The main purpose of this theoretical part, can be summerizing in two main aspects. First, is to making an theoretical overview of the modified electrode area, and secondly to target a theoretical base in terms of the materials that we used to prepared the modified electrode electrodes.

Were describes the procedures for modification of the electrodes surface using common substrates such as carbon paste electrode substrates and new generation type substrates like conducting polymers and micro and nanostructured inorganic modifying agent.

It was stressed the importance of using these new types of materials, the improvements that they bring in terms of electrochemical and catalytic properties and possible applications that these new molecular architecture can have. In order to link these theoretical aspects with the experimental, have described the electrochemical properties necessary for a material used in practical applications.

2. MODIFIED ELECTRODES

Modified electrode is an electrode made by a conducting or semiconducting material coated with a monomolecular or multimolecular ionic or polymeric layer with chemically modifing role, which investigated in electrochemicaly terms put in evidence chemical, electrochemical and optical properties different from the conventional unmodified electrode [1].

Some of the main advantages of the modified electrodes respecting to conventional electrodes are:

- Selective binding and preconcentration of an analyte in the modified layer;
- Electrocatalysis of some redox reaction in which the analyte have slow reaction capacity on the modified electrodes surfaces;
- Incorporation of some biomolecules, particularly enzymes, for biodetection;
- Permeoselectivity and barrier effects of interferent electroactive species and/or active species on the surfaces;
- Electrochemical detection of non-electroactive ionic analytes;
- Selective potentiometric response.

A modified electrode consists of two distinct parts: the surface of the support electrode and a layer of chemically modifing agent witch cover the electrode. Coupling this two components, namely immobilization the modifier on the electrode surface is designed to introduce the catalytic centers on the surface of a conducting or semiconducting material normally inactive. There are various options regarding the development of a modified electrode and various methods to attach the modifier, but important criteria in choosing are simplicity and reproducibility strategy to obtain a robust modified electrode. Thus, the coupling of two distinct components of a modified electrode, namely fixing the modifying species on the electrode surface, are based on the following immobilization methods:

(a) surface modification through covalent binding;
(b) surface modification by adsorption;
(c) surface modification with polymer film;

In practical experiments carried out by me in the thesis, I used a combination of these immobilization methods, summarized in the diagram below: I adsorbed the monomeric form of a conducting polymer on the surface of a conventional electrode, I electropolimerized this monomer on the surface of the electrode, so I modified a conventional electrode surface with a polymer layer. In some experiments, the polymer layer was functionalized polymer with carboxyl groups, then in three different ways, the functionality existing on the modified electrode surface can be coupled covalently with other species of interest.

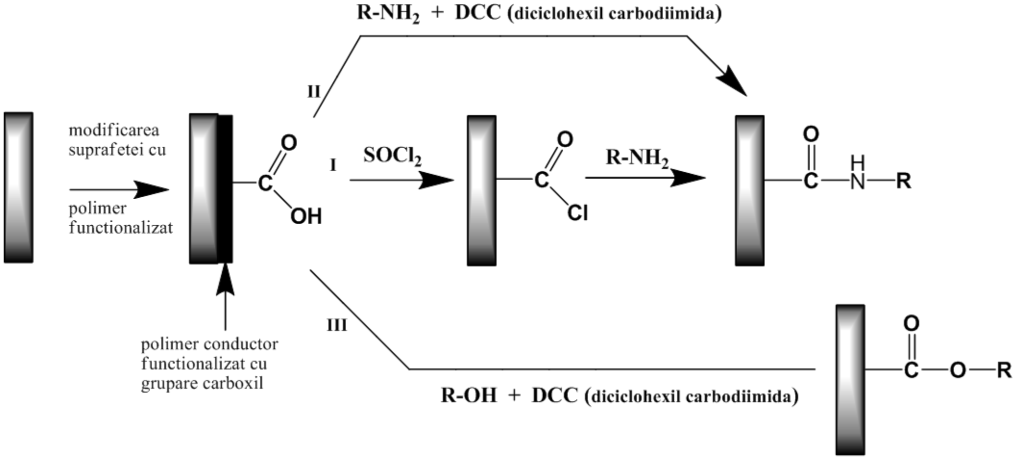

Figure 1. Modification of the surface by covalent coupling via carboxyl groups

The applications of the modified electrodes are very numerous, this is one of the reasons that modified electrodes have gained attention in electrochemical terms. Applications of modified electrodes are found in areas such as electrosynthesis reactions (stereospecific) electroanalysis (sensors) and electrocatalysis (fotoelectrocatalysis).

2. CONDUCTING POLYMERS

Conducting polymers are the most recent generation of polymers that offer an unique combination of properties that do not meet in any other known material, namely electrical and optical properties of inorganic semiconductors and mechanical properties and chemical variability of organic synthetic materials [2]. Conducting polymers have gained considerable interest as suitable matrices for biomolecules used in order to increase stability, response speed and sensitivity, which resulted in their use in more and more biotech and biomedical applications [3].

Electrochemical synthesis is the most commonly used method for obtaining conducting polymers, with the advantage of simplicity and the possibility of obtaining polymer films in different forms and architectures. Electrochemical deposition process allows to obtain layers with controlled thickness and different degrees of doping. Compared with other synthesis methods, with the electrochemical method can be obtain polypyrrole layers with highest conductivity values.

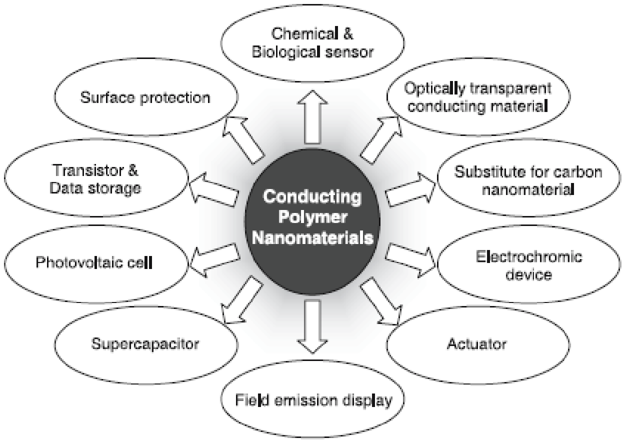

Figure 3. Application fields of conducting polymers

Electrochemical method is fast, clean (you can use water as a solvent), very accessible (does not require catalysts) to obtain conducting polymers.

Among the most popular applications of conducting polymers can remember sensor applications and enzyme biosensors [4] and imunosensors [5]. In addition to these classical applications, conducting polymers can be used in areas such as, transistors, data storage devices, supercapacitor, solar cells, electrochemical devices, actuators, transparent conductive materials, surface protection and substitutes for carbon materials. In Figure 2 are shown schematically some of the areas of applications of conducting polymers

PART TWO - ORIGINAL CONTRIBUTIONS

1. Polypyrrole

Polypyrrole (Ppy) is considered representative of the class of heterocyclic conducting polymers, one of the most commonly used conducting polymers in a wide variety of applications due to relatively good stability and the possibilities to synthezis as independent polymer layer, as copolymers and polymer composites [6].

The electropolymerization process of pyrrole can be described by a stepwise reaction mechanism involving monomer electrooxidation on the anode surface. In our experimets were used as synthesis methods the **galvanostatic deposition**, at constant current by monitoring the current density (j) the **potentiostatic deposition** at constant potential and **cyclic voltametry** by cycling the potential in a chosen field, at an optimal scan rate. The cyclic voltammetry experiments were used also for the electrochemical characterization of the polypyrrole layers.

a) The preparation of polypyrrole layers (PPy) under galvanostatic condition

This galvanostativ method, involves the application of a constant current for pyrrole oxidation. The main disadvantage is the impossibility of discrimination between the oxidation processes that occur in the potential arising during polymerization. This method allows to obtain large surfaces of the polymer as the most viable method for technological applications.

b) The preparation of polypyrrole layers under potentiostatic condition

The potentiostatic method allows the synthesis of polypyrrole layers at an optimal potential previously determined by cyclic voltammetry measurements. The main disadvantage of this method is limiting the sample to small areas, to avoid the effects of increasing the potential difference between reference electrode and working electrode. The preparation of the polypyrrole layers under potentiostatic condition were performed at a constant potential of 750 mV, applied for 150 seconds in phosphate buffer solution (pH = 7). The amperometric curve obtained from the preparation of the polypyrrole layers under potentiostatic condition is shown in Figure 3.

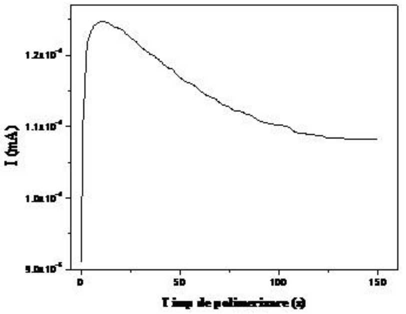

Figure 3. Cronoamperometric curve obtained from the preparation of the polypyrrole layers under potentiostatic condition.

c) The preparation of polypyrrole layers by cyclic voltammetry

The synthesis of polypyrrole layers by cyclic voltammetry was achieved by successive scans (5 cycles) carried out on the potential range - 1000 ÷ + 1200 mV at 50 mV/s scan rate. In the figure 4 is presented the cyclic voltamograms obtained on the electrodeposition of the polypyrrole layers from acetonitrile solution with 0.1 M pyrrole and 0.1 M LiClO4.

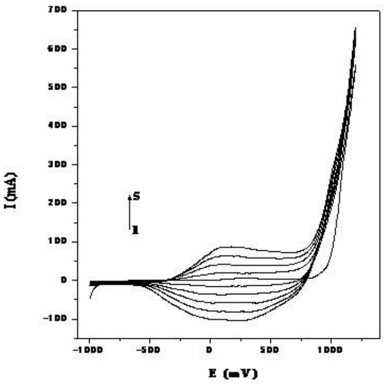

Figure 4. Cycling voltammograms obtained on the electrodeposition of the polypyrrole layers from acetonitrile solution ACN\LiClO$_4$;

For electrochemical characterization of the as prepared polypyrrole layers, cyclic voltammetry experiments were performed in the background electrolyte at different scane rate, between 10 mV / sec and 200 mV / s, the potential range - 200 and + 800 mV. The results lead to the following conclusions: Increasing the scane rate we observe an increases of the peaks intensity and an anodic peaks shift towards more positive values and the cathodic peaks to more negative values, which is equivalent to increase in absolute value the ΔEp, The increase the ΔEp value shows an increase in the irreversibility of the process with increasing the scane rate. The electrochemical parameters show that the electrochemical processes are monoelectronice, quasi-reversible, at lower scane rate, the anodic peak is almost the mirror image of the cathodic peaks (I_{pa} / I_{pc} ≈ 1). By ploting the peak intensity function of $v^{1/2}$ shows a linear dependence of the two parameters indicating that a diffusion mechanism is involved in the electron transfer by polypyrrole layer.

Morphological characterization of the polypyrrole layers

The characteristic morphology of the polypyrrole was investigated with scanning electron microscope (SEM) type JSM 5600 LV (JEOL company), equipped with EDX spectrometer (Oxford Instruments) for qualitative and quantitative microanalysis X-rays

In order to emphasize the effect of synthesis parameters on the morphology of polymer layers it was compared to samples prepared under different conditions, which we illustrate the effect of monomer concentration on the morphology of the as prepared polypyrrole layers.In this respect, two polypyrrole samples were compared ETS 8 with the monomer conc. 0.1 M and ETS18 with the monomer conc. 0.05 M, prepared electrochemically at j = 0.6 mA/cm^2. From Figure 5, notice that changing the concentration of monomer in solution induces significant differences in morphology of the polypyrrole layers reflected in electrical conductivity.

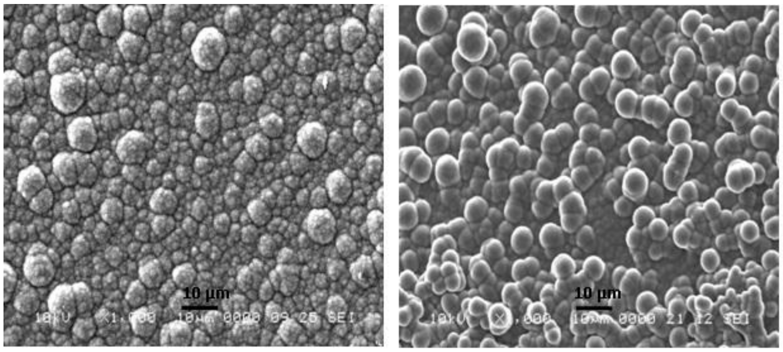

Figure 5.
Surface morphology of two samples prepared at different concentrations of polipirol (a) $c_{pyrrole}$ = 0.1 M (sample ETS 8, σ = 85 S / cm), and (b) $c_{pyrrole}$ = 0.05 M (sample ETS 18, σ = 38 S /cm).

The sample ETS8 prepared at optimum monomer concentration (0.1 M) have a compact globular structure with a relatively uniform distribution in terms of shape and size, with the size in the range 2-5 µm.

By the relative intensities of the X radiation spectrum and elemental analysis for these samples (Figure 6) was determine the doping ratio of the samples, using the ratio between atomic concentration of sulfur present in the dopant molecule (toluensulfonatul) and nitrogen present in the pyrrol ring : ETS 18 - S / N ratio = 0.20; ETS 8 - S / N = 0188.

Tabel 1.

The result of elemntal analysis with EDX spctrometer for the polypyrrole layer doped with toluensulphonic anions (sample ETS18)

Element	Conc. Aprox.	Corrected Intensity	Masic Percent (%)	Atomic Percent (%)
C	66.06	1.0991	55.48	63.17
N	3.29	0.7895	16.00	15.62
O	16.42	0.7176	21.11	18.04
S	7.79	0.9698	7.42	3.16
Total			100	

Tabel 2.

The result of elemntal analysis with EDX spctrometer for the polypyrrole layer doped with toluensulphonic anions (sample ETS8)

Element	Conc. Aprox.	Corrected Intensity	Masic Percent (%)	Atomic Percent (%)
C	52.82	1.0861	55.24	62.88
N	2.99	0.1896	17.88	17.45
O	11.78	0.6974	19.18	16.39
S	6.58	0.9703	7.70	3.28
Total			100	

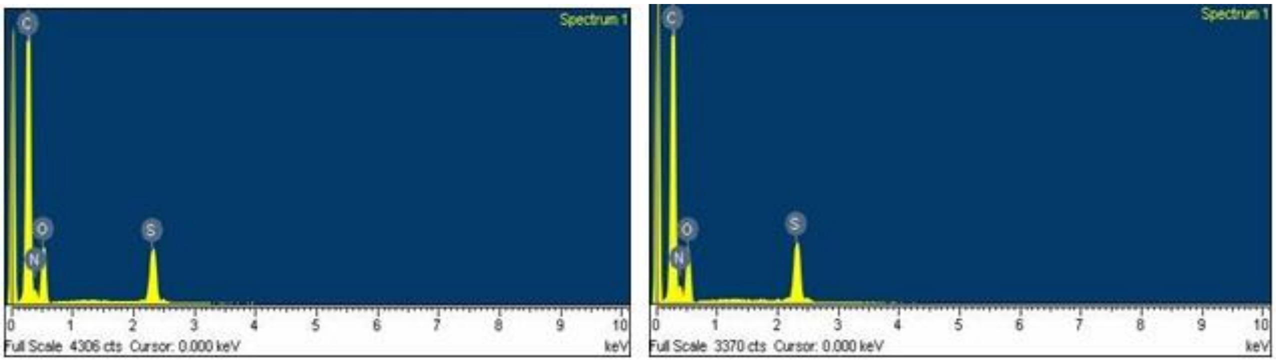

Figure 6. EDX spectrum for the polypyrrole layers doped with toluene sulphonic anions (a) sample ETS18 and (b) sample ETS8.

The similar values of the S/N ratio for the two samples shows that when used the same concentrations of doping ions in the polymerization solution are obtained samples with approximately the same doping degree, regardless of the concentration of monomer. Although the two samples have almost the same doping degree (the same concentration of charge carriers), they have very different electrical conductivity due to structural features. This means that the optimization of synthesis parameters is mainly to improve the structural properties of polypyrrole to increased the mobility of charge carriers. Sample ETS8 prepared at optimum monomer concentration (0.1 M) has a structure with lower concentration of defects compared with the sample ETS 18 prepared at lower monomer concentration (0.05 M).

Electrical caracterization

Effect of the synthesis conditions on the electrical characteristics of polipirolului

Of the many parameters that determine the electropolymerization process we focused on those that influence the structural and electrical properties of polypyrrole: nature and concentration of doping agent, polymerization current density, polymerization time, solvent, temperature.

The nature of doping ions is one of the most important factors for the structural morphology of the polypyrrole. Organic ions with aromatic type structure like toluensulphonic (TS^-) and naftalensulphonic (NS^-) induce the formation of a compact structure and relatively ordered chains in parallel planes with the electrode surface compared with smaller inorganic ions with spherical structure ($ClO_4^{\ -}$, BF_4^-).

The electropolymerization current density value, j, influences the growth rate of polymer layer on the electrode and the polymerization time determines the thickness of the polymer layer. These two parameters are not independent and also affects the polymer structure and the electrical conductivity.

Diagrams from Figures 7 (a, b) shows the variation of electrical conductivity with j for the polypyrrole layers doped with TS^- and NS^- ions, the concentration of doping ions in solution is the same, 0.01M. Small differences in conductivity are obtained in the range $0.6\ mA/cm^2 \leq j \leq 2$, this area representing favorable conditions to obtain layers with good electrical and mechanical properties. The electrical conductivity decreases significantly to low current density, $j = 0.2\ mA/cm^2$ and high values, $j = 4.2\ mA/cm^2$. The optimal value corresponding to the maximum value of σ is $j = 2\ mA/cm^2$ for the polypyrrole layers doped with TS^- and $j = 0.6\ mA/cm^2$ for polypyrrole layers doped with NS^-.

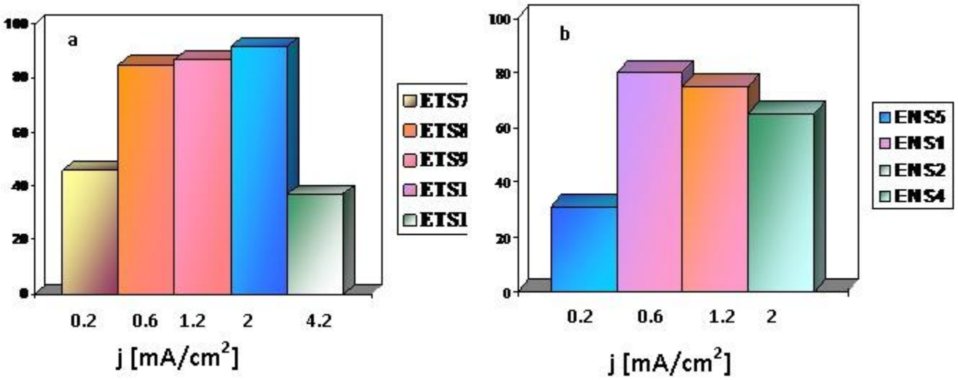

Figure 7. Variation diagrams of electrical conductivity with the polymerization current density for PPy doped with TS^- anions (a) and PPy doped with NS^- anions (b).

The stability of electrical conductivity for polypyrrole layers prepared under different conditions

One of the most important factors for stability of the electrical conductivity is the nature of doping ions. Significant differences in stability of electrical conductivity in time can be seen in Figure 8. for PPy layers prepared electrochemically with different types of doping ions (TS^-, ClO_4^-, BF_4^-). The degree of electrical conductivity stability in time decreases in the order $TS^{--} > ClO_4^- > BF_4^-$. Aromatic structure doping anions like (TS^-, DBS^-) are more stable under the action of oxygen in comparison with inorganic anions (ClO_4-, BF_4-) [7].

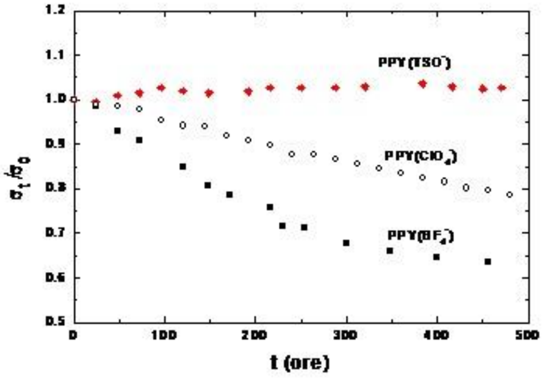

Figure 8. Variation of normalized electrical conductivity in time for polypyrrole synthesized by electrochemical method with different types of doping ion

Analysis of temperature dependence of electrical conductivity

It has made an analysis of the dependence of electrical conductivity with temperature. In this respect, it has made an extensive theoretical study of transport mechanisms in conducting polymers. The interfibrilar and intrafibrilar conduction process can occur through the following transport mechanisms [8]

- One-dimensional conduction along the chains by mobile charge carriers,
- Hopping between localized states on the chains,
- Tunneling between extending conductive areas from inside of fibrils.

Taking account the existence of areas with different electrical conductivity in real polypyrrole samples, it was examined the behavior of electrical conductivity with temperature, in the described charge transport models. Based on experimental data of variation of conductivity with temperature was made a parallel between thecharge transport models:

a. Charge transport by hopping on variable distance The Mott models.
b. Charge transport by tunneling.
c. The Zuppiroli models. Hopping between polaronic clusters.

The experimental data σ (T) for polypyrrole doped with different types of ion, having the electrical conductivity ≤ σ 40 S / cm, at room temperature, were fit both using charge transport by tunneling model and the model proposed by Zuppiroli. In Figure 9, experimental data are presented σ (T) and fit curves with a relation by the tunneling charge transport model, whene the variation of the electrical conductivity with temperature is according to a law of $\exp [- (T_0 / T)^{1/2}]$ type.

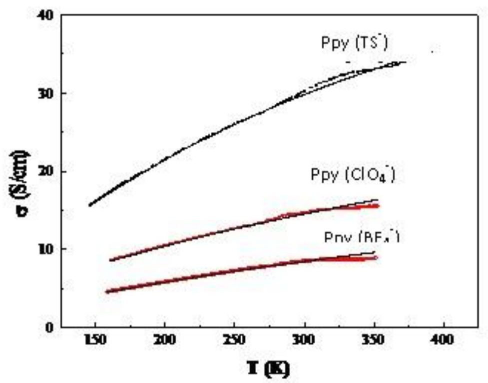

Figure 9. The experimental data of electrical conductivity variation with temperature (symbols) and fit curves (solid line) with the tunneling charge transport model for polypyrrole samples prepared electrochemically: PPY (TS^-) PPY (ClO_4^-), PPY (BF_4^-).

In the tunneling charge transport model, the values for the tunneling junction in polypyrrole samples PPY (TS^-) corresponding to about two rings of pyrrole (the monomer size is = 3.7 Å). For PPY (ClO_4^-) and PPY (BF_4^-) there is not a correlation between the values of electrical conductivity and width of tunneling junction. Experimental electrical conductivity data for samples were analyzed in the Zuppiroli model [9]. In this model, electrical conductivity varies with temperature according to a law of exp [- $(T_0 / T)^{1/2}$] type (Figure 10).

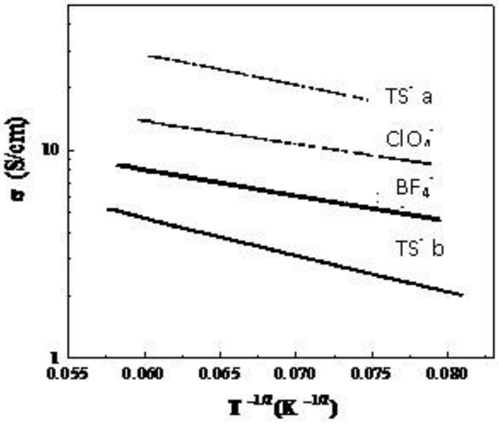

Figure 10. Variation of electrical conductivity with $T^{-1/2}$ in the Zuppirolli model for polypyrrole samples doped with different ions: PPY (TS^-) TS^- by toluene sulfonic acid electrolyte (HTSO); PPY (ClO_4^-), PPY (BF_4^-); PPY (TS^-)b TS^- by toluene sulphonate electrolyte (NaTSO).

Low values obtained for the distance between clusters suggests a very compact structure in polypyrrole. However we can not make a correlation between electrical conductivity values and fit parameters in the Zuppiroli model.

Conclusion

- Polypyrrole samples were prepared by three different synthesis techniques: galvanostatic deposition, potentiostatic deposition and cyclic voltammetric deposition. Based on morphological and electrical characterization of the as prepared samples we conclude that the samples obtained by the potentiostatic deposition techiques are the best, with good correlation between mechanical, electrical and structural properties. Also, the electrochemical response of these samples is reproductible and well defined;
- There have been drooling the synthesis conditions of the polypyrrole layers : monomer concentration, dopant type and concentration, polymerization time, supporting electrolyte. Following investigations have established the optimal synthesis parameters of polypyrrole layers;
- The morphology of the as prepared samples was investigated in order to determine the correlation between synthesis parameters and polypyrrole structure. It was observed that electrochemically prepared PPy samples, whether made under galvanostatic or potentiostatice condition presents a typical "cauliflower" type globular microstructure with the particles size in the range 1-5 μm.
- The electrical conductivity were measured for the samples prepared in galvanostatic condition and have established the correlations between synthesis parameters and conductivity. It was identified the optimum synthesis parameters for obtaining high electrical conductivity values ($\sigma = 113$ S / cm) and good stability for PPy.
- It was made an extensive documentary on the transport mechanisms in conducting polymers and develop an appropriate model to describe the conduction process in heavily doped PPy layers.

2. Functionalized polypyrrole

2.1. Amphiphilic polypyrrole

Amphiphilic pyrole monomer is a pyrole molecule functionalized with a linear chain having an ionic group at the end. Due to its special electrochemical properties this molecule has successfully been used in developing strategies for immobilization of enzymes, by adsorption of enzyme on electrode surface before the electropolymerization step of pyrole monomer [10].

In order to obtain the modified electrodes, the following stock solutions were prepared in advance: 6 mM amphiphilic pyrole solution in water, 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $FeCl_3$ in HCl 0.1 M + KCl 0.1 M, pH = 1.1.

More architectures of modified electrodes were made by alternating the order of deposition of the polymer and redox mediator, as follows:

(i) graphite / amphiphilic polypyrrole / Prussian blue (**G/PPy/PB**)
(ii) graphite / Prussian blue / amphiphilic polypyrrole (**G/PB/PPy**)
(iii) graphite / Mixture (Prussian Blue + amphiphilic polypyrrole) (**G/(PB+PPy**)

After obtaining the modified electrodes with the architectures listed above, they were characterized in terms of electrochemical properties, following the catalytic effect of each electrode used to reduce H_2O_2 by cyclic voltammetry.

In all three constructive variants the electrocatalytic characterization was performed to the modified electrodes thus obtained. Electrocatalytic characterization of modified electrodes aims electroreduction reaction study of hydrogen peroxide on obtained modified electrodes. Voltammetric responses for the three modified electrodes, in the absence and presence of different concentrations of H_2O_2, were recorded in order to study the performance of electrocatalytic effect of modified electrodes obtained in the three constructive variants for the electrocatalytic reduction of H_2O_2. Cyclic voltamograms were recorded in HCl 0.1 M + KCl 0.1 M solutions, pH = 3, containing H_2O_2 concentrations between 1 mM to 10 mM, at a scan rate of 20 mV/s (Figure 11. a, b, c).

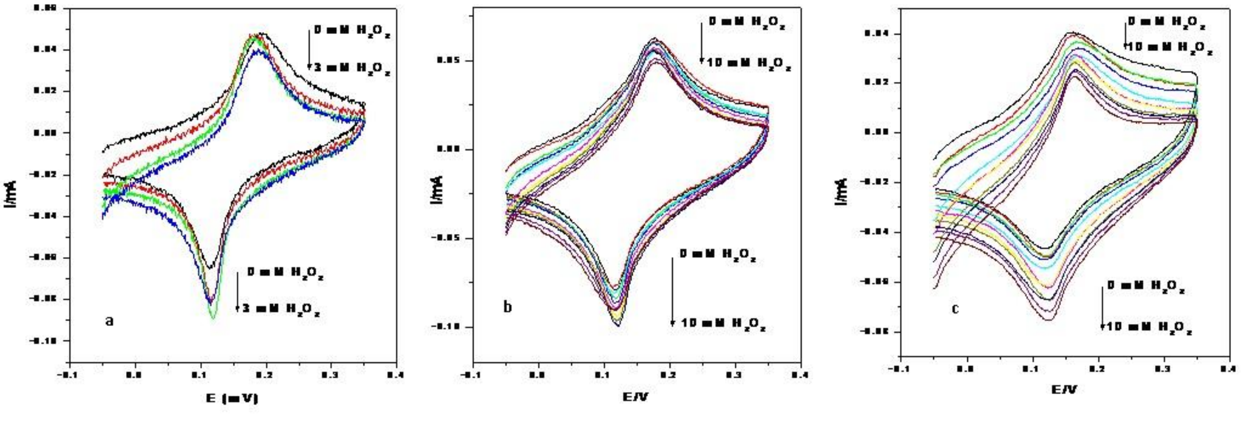

Figure 11. Electrocatalytic effect of modified electrodes in the absence and presence of different concentrations of H_2O_2: (a) **G/PPy/PB** (b) **G/PB/PPy**, (c) **G/(PB+PPy).**
Experimental conditions: scan rate 20 mV/sec, background electrolyte HCl 0.1 M + KCl 0.1 M, pH = 3.

Using cyclic voltammetry experiments performed in the presence of H_2O_2 at a relatively low potential scan rate, the electrocatalytic efficiency of the modified electrode with Prussian Blue and amphiphilic polypyrrole was estimated. Electrocatalytic efficiency value, obtained in the presence of 3 mM and 10 mM H_2O_2 concentration, and the value of calibration curves parameters of the for the three modified electrodes are given in Table 3.

Table 3. Calibration curves parameters for the modified electrodes

Modified electrode	**Electrocatalytic efficiency**		**R/nr points**
	H_2O_2 concentration		
	3 mM	**10 mM**	
G/PPy/PB	1.38	-	0.9537/4
G/PB/PPy	1.08	1.28	0.9926/11
G/(PB+PPy)	1.1	1.62	0.9886/11

Electrocatalytic efficiency values obtained in all three constructive types of modified electrodes with amphiphilic polypyrrole and Prussian Blue mediator, are relatively small compared to the literature. This behaviour indicates that obtained modified electrodes show an electrocatalytic effect on reducing H_2O_2 but not strong enough to be used in applications as sensors. Low electrocatalytic efficiency is because the mediator is adsorbed in insufficient concentration on the electrode surface; a major obstacles being the presence of amphiphilic polypyrrole layer hampering the diffusion of Prussian Blue mediator to the electrode, in all three variants. Electrocatalytic parameters can however be improved by adjusting the preparation conditions of modified electrodes and finding an optimal constructive variant.

Conclusions

- Three modified electrodes, with different molecular architectures, based on amphiphilic polypyrrole and Prussian Blue were prepared and characterized in terms of electrochemical behaviour;
- Electrochemical characteristics of the as prepared modified electrodes were studied comparative and also the molecular architecture effect on the electrochemical response;
- The electrocatalytic effect of modified electrodes obtained in three constructive variants for electrocatalytic reduction of H_2O_2 was studied by cyclic voltammetry experiments performed in the absence and presence of different H_2O_2 concentrations;
- The obtained electrocatalytic results are going to be improved by developing new constructive methods and modifying synthesis parameters of modified electrodes;
- As electrode materials, new obtained hybrid architectures are promising materials for applications in sensors field, but improvements regarding the thickness of Prussian Blue mediator layer adsorbed on electrode are needed in order to rise the electrocatalytic efficiency of modified electrodes thus obtained.

2.2. Functionalized polypyrrole with carboxyl groups

Functionalized conducting polymers are materials that specifically interact with different molecular or biomolecular species, depending on the nature of functional group existing in the structure. The easiest and most effective way to functionalize the surface of polypyrrole films is to use pyrrole monomers functionalized with carboxyl group (-COOH); this group can be easily modified later with various chemical or biological species. The main purpose of the experiments contained in this chapter has been the developing of new functionalized electrode materials based on homo- and co- pyrrole polymers, with carboxyl groups attached to the surface.

The following homopolymers were synthesized: polypyrrole (**PPy**), [poly(4-oxo(1H-pyrrole-3-yl) butanoic acide)] (**NPPy**) and [poly(3-(1-pyrrolyl) propanoic acide] (**3PPy**) and the following copolymers [poly(pyrrole-co-4-oxo(1H-pyrrole-3-yl)butanoic)acide)] (**PPy-NPPy**) and [poly(Pyrrol-3-(1-pyrrolyl) propanoic)co-acide] (**PPy-3PPy**).

Electrodeposition of functionalized polypyrrole layers was performed by two different electrochemical techniques: (a) potentiostatic and (b) cyclic voltammetry.

Electrodeposition of functionalized polypyrrole layers under potentiostatic conditions was made at constant potential 1080 mV *vs* Ag│AgCl/KCl$_{sat}$ for the homopolymer and copolymers based on **NPy**, and at constant potential 705 mV *vs* Ag│AgCl/KCl$_{sat}$ for the homopolymer and copolymers based on **3Py**, at different reaction times.

Electrodeposition of functionalized polypyrrole layers by cyclic voltammetry method

Functionalized polypyrrole layers were electrodeposited by cyclic voltammetry method, by cycling the potential in the range - 600 ÷ 1500 mV at a 50 mV/s scan rate from the specific synthesis solutions to each monomer separately.

Functionalized copolymers films were investigated by cyclic voltammetry in phosphate buffer solution pH=7. Voltamogramms were compared with the voltamogramms recorded for the **PPy** and **NPPy** homopolymers. From Figure 12, one can see that the electrochemical responses of copolymers (curves c, d, Figure 12) is intermediate the electrochemical responses of **PPy** homopolymer (curve a, Figure 12) and **NPPY** (curve b, Figure 12), indicating that the **NPy** substituted monomer was incorporated into the copolymer structure. It may be also noted that **PPy-NPPy** copolymer (curves c, d, Figure 12) shows a quasi-reversible pair of peaks, positioned at + 54 mV and + 350 V *vs* Ag│AgCl / KCl$_{sat}$, while **PPy-3PPy** copolymer (curve e, Figure 12) shows only an oxidation peak at + 680 mV *vs* Ag│AgCl / KCl$_{sat}$, this behaviour is due to structural unevenness observed in **PPy-3PPy** copolymers films.

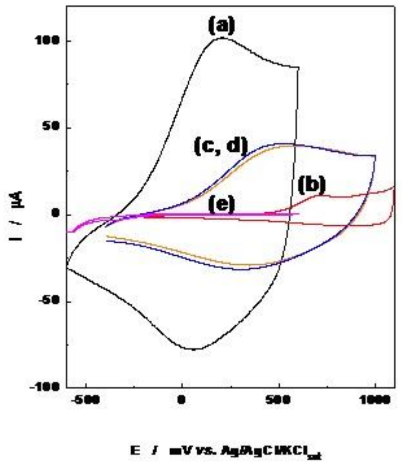

Figure 12. Cyclic voltamogramms for: (a) **PPy** homopolymer, (b) **NPPy** homopolymer (c) **PPy-NPPy** with **Py:NPy** = 5:1 copolymer, (d) **PPy-NPPy** with **Py:NPy** = 3:1 copolymer, (e) **PPy-3PPy** copolymer.

To confirm the structure formation of **PPy-NPPy** copolymer films, FT-IR spectroscopy measurements were carried out on the glassy carbon electrode surface. FT-IR spectra were recorded for **PPy** and **NPPy** homopolymers and **PPy-NPPy** copolymer at different monomer ratios 5:1 and 3:1 (Figure 13).

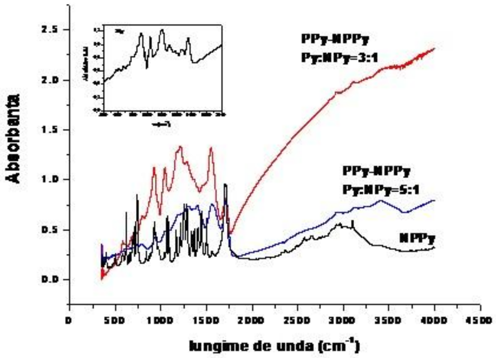

Figure 13. FT-IR spectrum of **PPy** (inset), **NPPy** homopolymers and **PPy-NPPy** copolymer with **Py:NPy** ratio 5:1 and 3:1

Characteristic polypyrrole morphology was investigated with a scanning electron microscope (SEM) JSM 5600 LV type (JEOL company), equipped with EDX spectrometer (OXFORD Instruments) for qualitative and quantitative microanalysis with X rays. Recorded SEM images on two samples of polipirole functionalized with **NPy** and **3Py** monomers show a significant difference between the structures of the two copolymers (Figure 14).

In both samples one can see a combined structure, in which the two-dimensional base consists of a uniform structure, of "cauliflower" type, characteristic for the unsubstituted polypyrrole with feature size of 1-2 µm, having on the surface three dimensional growths, of globular type, caused by two functionalized monomers. A more rigorous ordering is noted in case of using the **NPy** monomer, in which case the three-dimensional surface formations have a relatively narrow size distribution with average size about 5-10 µm; these formations do not aggregate and distribute evenly throughout film surface. In case of polypyrrole copolymerised with functionalized **3Py** monomer a relatively disordered structure, due to the large aggregates that are formed on the base surface of the polypyrrole film; the aggregates form islands with sizes ranging from 1-50 µm.

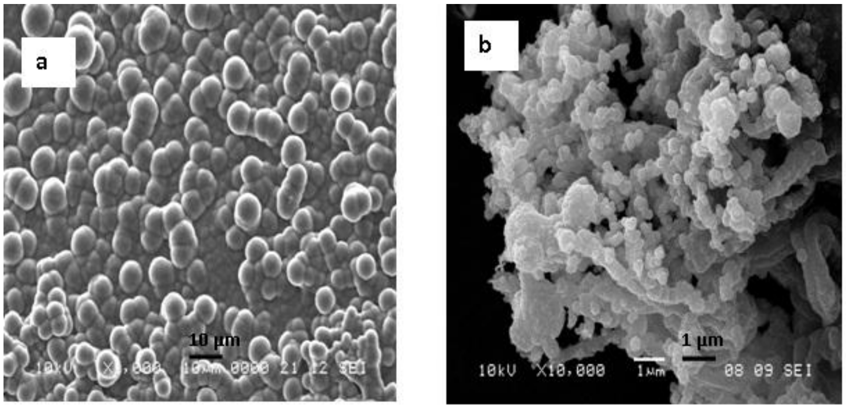

Figure 14. Morphology of polymer films (a) functionalized polypyrrole of **PPy-NPPy** type and (b) functionalized polypyrrole **PPy-3PPy** type

Obtained copolymers films with carboxyl groups grafted on the surface were used to immobilize on the surface some redox mediators for the development of modified electrodes with special architecture, for electrocatalysis species of interest such as NADH or H_2O_2. Redox mediator used was elected from phenothiazines class namely Toluidine Blue.

Oxidative electropolimerization of Toluidine Blue mediator takes place on the surface of functionalised polypyrrole deposit before, using a method reported in the literature [11], which consists in potential cycling in the field potential between -600 and 800 mV *vs.* Ag | AgCl / KCl$_{sat}$ at a scanning srate of 50 mV/s, 20 cycles, in borate buffer solution with pH=9.1 and containing 0.1 M NaNO$_3$ and 0.4 mM TB (Figure 15).

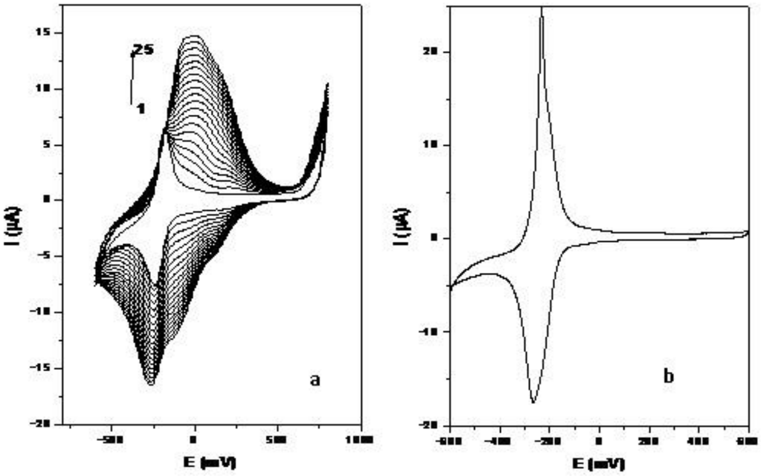

Figure 15. Cyclical voltamogramme characteristic for TB (a) electropolimerization at the surface of functionalized polypyrrole, (b) testing of modified electrode with TB in phosphate buffer;

Covalent attachment of Toluidine Blue mediator through the carboxyl groups existing at the surface of polypyrrole layer

When TB is immobilized by electropolymerization at the polypyrrole modified surface, the obtained modified electrode has a relatively electrochemical unstable behaviour. As a result after multiple cycling in buffer solution, a colour change occurs near the electrode, which shows that some of TB found on the surface of modified electrode migrates in the electrolyte solution.

Research conducted within this thesis, regarding Toluidine Blue mediator immobilization by covalent attachment on the modified polypyrrole surface; represent a new and efficient strategy for the development of modified electrodes with relatively better stability. Covalent attachment of the Toluidine Blue mediator on the surface of functionalized polypyrrole layer is achieved by coupling the primary amino group, surface situated in position 3 of phenothiazine aromatic cycle, with carboxyl groups situated at the functionalized polypyrrole surface.

Figure 16 represents a cyclic voltamogramme of the modified electrode, recorded after covalent attachment of TB, in phosphate buffer solution, pH = 7 at a scanning speed of 50 mV/s. From this figure, we can see that the pair of redox peaks that appear in case of electrode modified by covalent binding of TB on the functionalized polypyrrole surface, is similar to that recorded for electropolymerizated TB on the surface of functionalized polypyrrole (Figure 15).

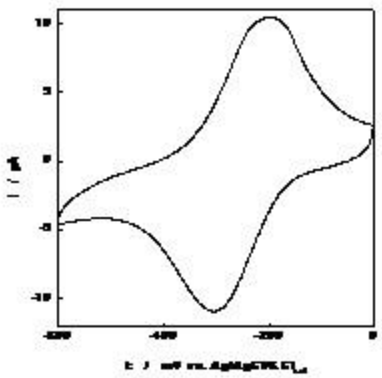

Figure 16. Cyclic voltamogramme feature of modified electrode after the covalent binding of TB at the surface of functionalized polypyrrole.

Compared with TB electropolymerization, covalent attachment of its amino group through the carboxyl groups existing on the surface of modified electrode generates a more stable modified electrode.

Taking into account the favourable electrochemical behaviour of modified electrode with functionalized polypyrrole and Toluidine Blue mediator covalently coupled to the surface of polymer layer, the electrocatalytic activity of the electrode to NADH was tested. To this end the voltammetric response of this electrode was recorded in the absence and presence of various NADH concentrations. The result is shown in Figure 17.

It is noted that in the presence of NADH, the anod current increases, indicating an electrocatalytic effect but not very significant which can not be estimated due to redox peak deformation.

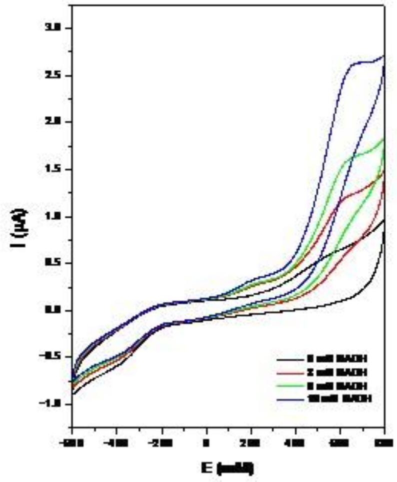

Figure 17. Cyclic voltamogramms of electrode modified with functionalized polypyrrole and Toluidine Blue mediator in the absence and presence of several concentrations of NADH

Research on this type of change are in progress in order to demonstrate the versatility of this method of restraint for immobilizing other redox mediators and/or enzymes and electrocatalytic effect testing for amperometric detection of some important analytes for biomedical applications and biotechnology.

Conclusions

- Two modified electrodes were obtained based on co-polymer layers containing pyrrole and functionalized pyrrole monomers with carboxyl groups grafted on pyrrolic ring;
- To optimize the co-polymer layer preparation, we studied the effect of synthesis parameters on the electrochemical response of obtained modified electrodes;
- PPy-NPPy copolymer deposited on the surface of glassy carbon electrodes acts as an anchor for covalent immobilization of Toluidine Blue, by coupling aromatic amine groups from position 3 of TB with carboxyl groups of functionalized polypyrrole;
- The covalent binding of TB on the functionalized polypyrrole surface, generates a more stable modified electrode, which has better electrochemical activity compared to that of electrode obtained by TB electropolymerization on the surface of modified polypyrrole.
- Electrocatalytic activity of modified electrode with functionalized polypyrrole and Toluidine Blue mediator at NADH was tested, observing a slight electrocatalytic effect, which can be exploited in further research.

3. Composite electrode materials based on carbon paste

Account the remarkable ability of carbon nanotubes to promote electron transfer in the electrochemical oxidation of NADH [12], in the research made in this chapter has examined the influence of single wall carbon nanotubes (SWCNT) on the oxidation of NADH in carbon paste type electrode, incorporating MB or MG mediators in synthetic zeolites. The new electrode materials (MB-Z-SWCNT-CPE, MG-Z-SWCNT-CPE) were compared with similar electrode materials in carbon paste and Sigradure K (MB-SK-CPE-Z, Z-SK-MG-CPE). Were carried out cyclic voltammetry measurements and rotating disk electrode measurements in different experimental conditions (different pH values, or different concentrations of NADH) to compare the sensitivity of SWCNT-based electrode with the electrode based on SK.

In this way, zeolite (50 mg) was modified with MB and MG by mixing the zeolite with an 0.01% aqueous solution (50 ml) of mediators, for 2 hours under magnetic stirring. The as modified zeolite, MB-Z or MG-Z was filtered, washed and dried. The modified electrodes MB-Z-Z-MG-CPE and CPE were prepared by mixing 25 mg of modified zeolite with Sigradure K powder (1 / 1, w / w) or SWCNT (2 / 1 w / w) and 10 or 20 ml of paraffin oil. The resulting paste was introduced into the cavity of the end of a Teflon tube. Electrical contacts were made through copper wires connected to the carbon paste The FTIR spectra (Figure 18) confirmed the successful formation of the composite material.

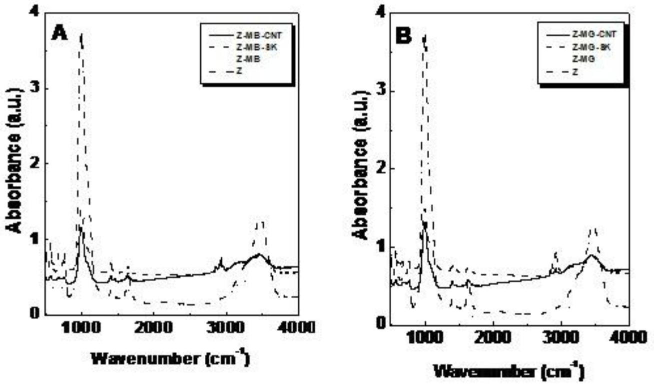

Figure 18. FTIR spectra of pure zeolite and composite materials based on MB (A) and MG (B).

In order to investigate the influence of SWCNT on the electrochemical behavior of modified electrodes cyclic voltammetry measurements were carried out on four electrodes: MB-SK-Z-CPE, MB-Z-SWCNT-CPE, MG-Z-SK-CPE, MG-Z -SWCNT-CPE. By the cyclic voltamograms for all four electrodes a pair quasi-reversible of peaks observed (Figure 19). It is important to note that the values of formal standard potential (E0 ') are shifted to more negative potential values compared with the values of the standard potential recorded for free MG and MB mediators in solution [13, 14].

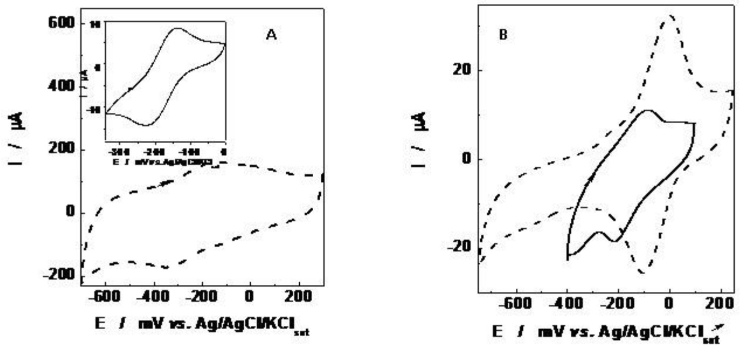

Figure 19. Cyclic voltamograms recorded on electrodes: MG-Z-CPEs (A) MB-Z-CPEs (B), for Sigradur K (-) and SWCNTs (---).

This behavior, the shift of the the standard formal potential to more positive values for mediator MB mediator compared with the shift to more negative values for MG mediator, could be attributed to a stronger interaction between the mediator MG and negatively charged zeolite matrix unless the mediator MB.

From the variation of the peak potential whit the scan rate (Figure 20), using the treatment proposed by Laviron [15] were estimated the rate constants for heterogeneous electron transfer process (k_s, s^{-1}) for all four modified electrodes. Surprisingly, it was observed that both mediators incorporated into the paste electrode based on SK has higher k_s values than thatobserved for the SWCNT based electrodes. Moreover, the values of k_s for electrodes modified with MB is higher than the corresponding value for the modified electrodes with MG. On the other hand, the k_s values increase with the decreasing of the pH, while the transfer coefficient (α) does not change significantly with the pH variation. Ks values determined for these systems are of the same order of magnitude as those reported in the literature [16]

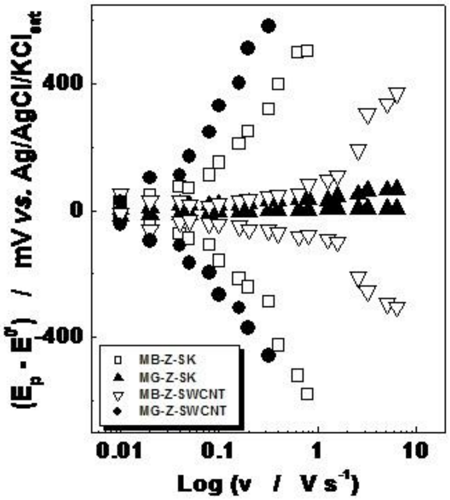

Figure 20. Experimental dependence of (E_p - E^0 ') with the logarithm of scane rate for the investigated carbon paste electrodes.

In the case of SWCNT-based modified electrodes, their formal potential is pH dependent, as expected for a redox process involving proton transfer. In contrast to this behavior, the formal potential of the two electrodes based on SK is particularly independent of pH. This behavior can be discussed in terms of existing interactions in heterogeneous system mediator -zeolite-electrode material.

In the pH range between 2 and 7, there is not observed dependence of $E^{0'}$ value with the pH in the MB-SK-CPE or SK-MG-S-CPE electrodes (Figure 21). This behavior is similar to that observed for carbon paste electrodes modified with MG adsorbed on the same type of zeolite, but using graphite as electrode material [17]. However, for the pH values higher than 7, both mediators have pH dependence, specific behavior for a redox process involving the transfer of 2 e^-/ 1 H^+ (ca. 30 mV / pH), the same behavior reported in the literature for MB mediator [18] and the MG mediator adsorbed on solid graphite electrodes in the same pH range [18].

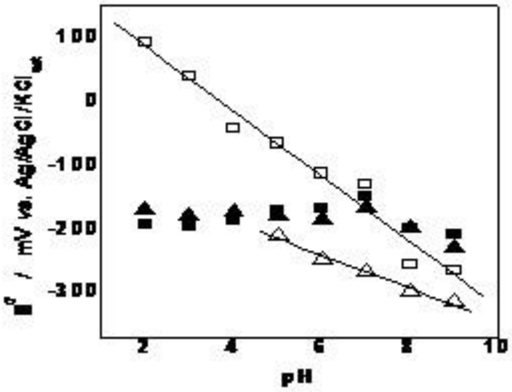

Figure 21. Dependence with the pH for the electrodes: MB-Z (■, □) and MG-Z (▲, Δ) for Sigradur K (■, ▲) and carbon nanotubes (□, Δ).

Surprising when SWCNT carbon nanotubes are used as electrode material for carbon paste electrodes modified with MB and MG adsorbed in zeolite matrix, throughout the pH range investigated (2-10) values the formal standard potential $E^{0\,'}$ are pH dependent. For the electrode MG-Z-SWCNT-CPE was determined a slope of 26 mV / pH throughout the pH range investigated (2-9), suggesting a transfer of 2 e^-/ 1 H^+. On the other hand for the MB-Z-SWCNT-CPE electrode is observed two different slopes, one at 68 mV / pH in the pH range 2-4 and another slope of 30 mV / pH in the pH range between 4 - 7. This behavior is very similar to that observed when the mediator MB is adsorbed on solid graphite electrodes [251], suggesting that the pH range 2-4 there is a transfer of 2 e^-/ 2 H^+, while at pH higher than 4, there is a transfer of 2 e^-/ 1 H^+. At pH 8 and 9 the cyclic voltamograms did not have a acceptable form, for the certainty evaluation of the formal standard potential value $E^{0\,'}$, so it did not take into account the values of $E^{0\prime}$ at these pH values. This is why the formal standard potential value at pH 8 and 9 were not included in the graph, nor served to calculate the number of electron and proton transfer. The different behavior observed for the carbon paste electrodes havong adsorbed two different mediaors into the zeolite matrix, is the result of local interaction between the mediator, zeolite and electrode material.

Electrocatalitical oxidation of NADH on modified carbon paste electrodes

Electrocatalytic oxidation reaction of NADH on the carbon paste electrodes Z-MB-SK-CPE, MB-Z-SWCNT-CPE, SK-MG-Z-CPE, MG-Z-SWCNT-CPE was identified by a clear increase of the anodic peak intensity in the presence of NADH and decreasing of the cathodic peak intensity (Figure 22). [19, 20]. Electrocatalytic efficiency, estimated as the ratio ($I_{[NADH] \neq 0}$ - $I_{[NADH] = 0}$) / $I_{[NADH] = 0}$ for 2 mM NADH, decreases in the order MG-Z-SWCNT-CPE (306%)> MB -Z-SWCNT-CPE (112%)> Z-SK-MG-CPE (39%)> MB-SK-Z-CPE (18%). One can see that SWCNT based modified electrodes have a better electrocatalytic efficiency towards NADH than those based on SK.

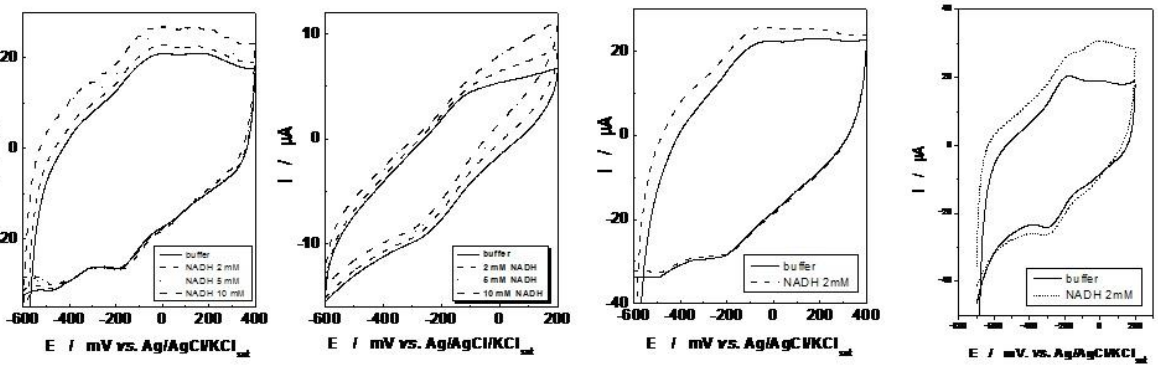

Figure 22. Cyclic voltamograms recorded for (a) MB-SK-Z, (b) MB-Z-CNT, (c) MG-Z-SK, (d) MG-Z-CNT, in phosphate buffer solution at pH 7 in the absence and presence of different concentrations of NADH, scae rate 10 mV / s.

In order to investigate the mechanism and kinetics of electrocatalytic oxidation reaction of NADH on carbon paste electrode modified with MB and MG, were made rotating disk electrode measurements at different concentrations of NADH and different pH values. Graphical representation of the Koutecky-Levich equation [19, 20], 1 / I vs. $\omega^{-1/2}$, allowed the calculation of k_{obs} values for electrocatalytic oxidation of NADH. Figure 23 shows the graphical representation of Koutecky-Levich equation for all four investigated modified carbon paste electrode. K_{obs} values depend strongly on the concentration of NADH. This was observed for most modified electrodes used for the electrocatalytic oxidation of NADH [21, 22], and can be explained by the formation of a complex charge transfer (CT) before the reaction products.

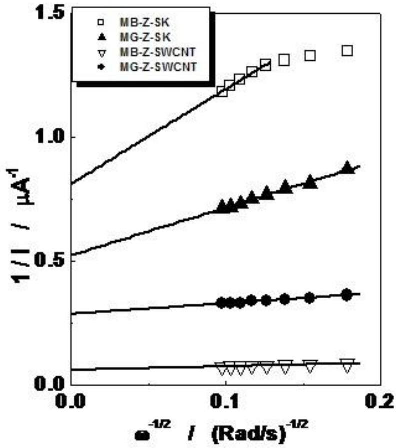

Figura 23. Graphical representation of Kouecky-Levich for modified carbon paste electrodes

Graphical representation of $1/k_{obs}$ vs. [NADH] shows in all cases a linear dependence between the two parameters, supporting the idea of forming a charge transfer complex (CT) between the mediator and NADH. By extrapolation to zero concentration of NADH ([NADH] = 0) were estimated Michaelis-Menten constant values (K_M) for all four electrodes. Using amperometric measurements performed in optimal experimental conditions, the amperometric response was recorded for all four modified carbon paste electrode to increase the concentration of NADH. By fitting the amperometric calibration curves with Michaelis-Menten equation, it were found the kinetic parameters K_M and I_{max} for all four modified carbon paste electrode. The linearity range (over 0.1 mM), the detection limit (~ 0.1 mm calculated from the signal – noise ratio), sensitivity and response time (less than 2 s) recommended the electrodes MB / MG-Z-SWCNT -CPE as amperometric sensor for NADH detection.

Conclusion

- In this chapter new electrode materials were prepared (MB-Z-SWCNT-CPE, MG-Z-SWCNT-CPE) based on SWCNT. The new electrode materials were compared in terms of electrochemical and electrocatalytic behavior with similar electrode materials consisting of carbon paste and Sigradure K (MB-SK-CPE-Z, Z-SK-MG-CPE)
- Also, in the research made in this chapter has reported the influence of single wall carbon nanotubes (SWCNT) on the oxidation of NADH in carbon paste electrode type, incorporating MB or MG mediators in synthetic zeolites.
- Cyclic voltammetry measurements and rotating disk electrode measurements have performed in different experimental conditions (different pH values, or different concentrations of NADH) to compare the sensitivity of SWCNT-based electrode with the electrode based on SK.
- It was concluded that SWCNT increases the affinity of the mediator to NADH and sensitivity too of the modified carbon paste electrode, regardless of the mediator. All four modified carbon paste electrodes can be used as sensors for NADH.

FINAL CONCLUSION

In this PhD thesis have been developed new advanced composite electrode materials with high-performance features and parameters. The new electrode materials were obtained by combination OF conducting polymers, such polypyrrole and / or functionalized polypyrrole with inorganic materials such as zeolites or carbon nanotubes and presents fundamental interest of new physical processes and phenomena induced by yhe nanostructuring of conducting polymers, interface effects, specific interactions between components, and applicative interst for a variety areas: actuators, electronic devices, chemical sensors, biosensors.

This doctoral thesis has as main objective to obtain new modified electrode architectures using next-generation substrate materials such as conducting polymers like polypyrrole or functionalized polypyrrole and development of new composite electrode material using inorganic modification such as zeolites or carbon nanotubes. The complex physico-chemical characterization of the electrode materials, led to a better understanding of the properties that they own, offering a wide perspective of applications in various fields, especially in bio electroanalytic.

- In the chapter "**Micro and nanostructured polymeric electrode materials based on polypyrrol"** new modified electrode materials were prepared using simple or functionalized polymer layers based on polypyrrole. It was made a complex physico-chemical characterization of this materials using modern techniques such as FTIR spectroscopy and scanning and tunneling electron microscopy. Also, the as prepared materials were characterized in electrical, electrochemical and catalytic terms. Based on the fact that the functionalized polypyrrole deposited on the glassy carbon electrode surface acts as an anchor for covalent immobilization of special interest groups, it was coupled aromatic amine groups in the 3 position of TB mediator with the carboxyl groups of the functionalized polypyrrole. It was obtain in this way a more stable modified electrode, which has better electrochemical activity compared to the modified electrode surface obtained by electropolymerization of the TB on the polypyrrole surfaces.. Based on promising obtained results, in the future will be develop sensors and biosensors using new obtained hybrid architectures.
- In the chapter "**Composite polymeric electrode materials based on polypyrol**" were prepared new composite electrode materials, by associating the organic conducting polymeric layers such as polypyrrole with inorganic micro and nanostructures like zeolites and carbon nanotubes. The as prepared materials were characterized in physico-chemical terms. The morphological characterization demonstrated the successful formation of polypyrrole- carbon nanotubes, respectively polypyrrole - zeolite hybrid structure. As future prospects, it will seek to improve the synthesis methods of this new molecular architectures mentioned above in order to obtain modified electrodes based on polypyrrole layers with relatively better electrochemical properties. It will be study the electrocatalytic properties of the modified electrodes thus obtained, to different analytes of interest for biomedical and biotechnological applications.
- In the chapter "**Composite electrode materials based on carbon paste**" were obtained new modified electrode assemblies using common materials such as carbon paste in combination with micro and nanostructures such as inorganic zeolites and carbon nanotubes, which were compared in terms of electrochemical and electrocatalytic behavior with similar electrode materials consisting of carbon paste and Sigradure K. It was concluded that SWCNT increases the affinity of the mediator to NADH and the sensitivity of the modified carbon paste electrode, regardless of the mediator. All four modified carbon paste electrodes can be used as sensors for NADH.

Based on the obtained results in the three major chapters of this thesis, I consider that this doctoral thesis approached and realise all objectives, while opening the possibility of implementing the new obtained materials in various applications like sensors or biosensors.

BIBLIOGRAFIE

1. Shaw B.R., *Electrochemistry*, Past and Present, ACS Symposium Series, 390, editors: J.T.Stock, M.V.Orna, American Chemical Society, Washington, **(1989),** 318.
2. Heeger A.J. et al., http:/www.nobel.se/chemistry/laureates/2000.
3. Adeloju S.B., *Analyst* 121 **(1996)**, 699.
4. Trojanowicz M., Krawczynski vel Krawczyk T., Alexander P. W., *Chem. Anal*. (Warsaw) 42 **(1997)**, 199.
5. Trojanowicz M., Krawczynski vel Krawczyk T., *Mikrochim.Acta* 121 (1995), 167.
6. Handbook of Organic Conductive Molecules and Polymers, Ed. H.S. Nalwa vol.2 **(1997)**, 416
7. Brie M., Turcu R., Mihut A., *Materials Chemistry and Physics* 49 **(1997)**, 174.
8. Turcu R., Neamtu C., Brie M., *Materials Science Forum* 122 **(1993)**, 83.
9. Zuppiroli L., Bussac M.N., Paschen S., O Chauvet., Forro L., *Phys. Rev. B* 50(8), **(1994)**, 5196.
10. Bussac M.N., Zuppiroli L., *Phys. Rev. B* 49(9), **(1994)**, 5876.
11. Zelikin A., Shastri V.R., Langer R., *J. Org. Chem*., 64, **(1999)**, 3379.
12. Kubota L.T., Muntean F., Roddick-Lanzilotta A., McQuillan A.J., L Gorton., *Quim. Anal*. 19 **(2000),** 15.
13. Munteanu F.D., Kubota L.T., Gorton L., *J. Electroanal. Chem*. 509 **(2001)**, 2
14. Gorton L., *J. Chem. Soc. Faraday Trans*, 82 **(1986),** 1245.
15. Labo M.J., Miranda A.J., Tunon P., *Electroanalysis* 9 **(1997)**, 191.
16. Bremle G., Persson B., Gorton L., *Electroanalysis* 3 **(1991)**, 77.
17. Ashok Kumar S., Chen S.M., *Sensors* 8 **(2008)**, 739.
18. Zhu L., Zhai J., Yang R., Tian C., Guo L., *Biosensors and Bioelectronics* 22 **(2007)** 2768.
19. Laviron E., *J. Electroana. Chem*. 101 **(1979)**, 19.
20. Curulli A., Carelli I., Trischitta O., Palleschi G., *Talanta* 44 **(1997)**, 1659.
21. Persson B., Gorton L., *J. Electroanal. Chem*. 292 **(1990)**, 115.
22. Walcarius,A. Lamberts L., Derounare E.G., *Electroanalysis* 7 **(1995)**, 120.