ACADEMIA ROMÂNĂ
SCOSAAR

Anexa nr.6

ABSTRACT OF HABILITATION THESIS

TITLE: ADVANCED MATERIALS WITH APPLICATIONS IN INDUSTRY AND ENVIRONMENTAL PROTECTION

Domeniul de abilitare: ***Chimie***

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This habilitation thesis entitled "ADVANCED MATERIALS WITH APPLICATIONS IN INDUSTRY AND ENVIRONMENTAL PROTECTION" summarizes my activity after defending the doctoral thesis and receiving the scientific title of Doctor in the field of Chemical Engineering based on Order no. 3876 of 19.06.2004 issued by the Ministry of Education and Research.

The scientific research activity that is the subject of this thesis includes two of the main research directions related to obtaining nanostructured polymers with special properties and to the study of the corrosion processes of iron and iron alloys, in the presence of inhibitors such as organic phosphorus compounds.

The research themes were based on a goal, that of limiting or better said to protect protecting the natural resources, which are essential to maintain our rhythm of life. Natural resources are not inexhaustible, they are decreasing and as a result, measures are required to reduce the lost in exploitation, to find suitable alternatives. Intrinsic conductive polymers, also known as "synthetic metals", have opened a new optimistic field of study in the replacement of classical metallic conductors. These polymers possess the typical advantages of polymers: low density, easy processing (in foils, films or wires), advantageous price, but also those brought by the metallic character, electrical, electronic, optical and magnetic properties. As a result, the research addressed concerned a current and intensively studied field: the field of polymers with special properties, polymers also known as synthetic metals. Besides these possible substitutes for metals, another research theme aimed to protect metals, especially of the iron and its alloys, to inhibit their corrosion and to extend the life of metal structures for industrial or civil consumption. For this purpose, organic compounds were tested as potential absorbing agents, as well as organic films.

The thesis is structured in two sections:

• *Section I* presents the important scientific achievements in the addressed research fields, based on the results of ten selected ISI works;

• *Section II* presents the most important professional results obtained after the doctorate and up to now: 80 articles published in ISI indexed journals (h-index 16), 4 books and 3 book chapters, project responsible for 2 research projects and member of the research team in 11 projects. In this habilitation thesis, the work performed by the candidate is presented in the current context of scientific research in the field, on an international level, emphasizing, in a documented way, the importance and novelty of her contributions. In addition, academic and professional achievements are presented, such as the coordination of research, project management, coordination of PhD theses, revision and editorial activities. These demonstrate a good capacity of the candidate to manage a research team organization and to supervision of didactic activities.

Section I includes the main scientific achievements in the field of research, structured in 2 chapters:

• contributions to the synthesis, characterization and applications of conducting polymers;

• contributions to the study of the anticorrosive properties of organic compounds with phosphorus.

Chapter 1 presents research directions that were initiated in collaboration with the Polytechnic University of Timisoara. The purpose of the research was to analyze some theoretical aspects regarding, on the one hand, the basic principles of charge transport in polymers, and on the other hand the chemical and electrochemical synthesis and applications of conductive polymers.

Subchapter 1.1 describes the importance and current state of research in the addressed research field. Subchapter 1.2 presents the studies carried out for the synthesis of polyaniline (PANI) with a nanofibrillar structure. The factors that affect the PANI morphology are analyzed separately, to find the conditions that generate the fibrillary morphology. The influence of the nature of the electrode and the supporting electrolyte system on the electropolymerization process of aniline (acid concentration and monomer/acid molar ratio and the nature of the metal substrate). The results demonstrated that PANI nanofibers could be obtained electrochemically on a variety of electrode materials, under specific conditions for each substrate (nickel, skeleton nickel and niobium). The morphological changes induce different properties of the polyaniline films. Films deposited at lower scan speeds show high values of surface-related capacitances, due to the increase in both thickness and electrochemically active surface, and are assumed to originate from an optimal combination of intra-chain and inter-chain charge transport. The nanostructured PANI films obtained have much higher values of the capacitance than those with a granular structure, which suggests a capacity of the PANI films to store electric charges. In the electropolymerization reaction, the aniline concentration has little effect on the PANI structure, only the thickness of the film increases with the increase of the aniline concentration. The PANI films obtained in solutions with a low acid concentration show a heterogeneous nucleation, and films with a granular morphology similar to corals. At large aniline/acid molar ratios, the polymer film deposited on the electrode present a lower, compact layer and an upper layer composed of short, highly branched nanofibers and granular particles. At high acid concentrations, the PANI film shows a clear nanofibrillar structure. The temperature influences the electrical properties of the films. The PANI film deposited on Pt is in a conductive state in the entire studied potential range, and with the increase in temperature, the conductive range becomes limited between 0.3 and 0.5 V.

Subchapter 1.3 presents the applications of PANI synthesized on various electrodes such as Ni, skeleton Ni and Nb, as well as chemically synthesized PANI. It was studied the possibility of using PANI but also polyaniline with boronic functional groups (PABA) for a variety of purposes. These include the creation of sensors for: various analytes (for dopamine biosensors), for dyes adsorption, for the improvement of the characteristics of solid electrolytes for dry batteries and for the catalytic effect for the evolution of the hydrogen evolution reaction (HER). The results obtained on the skeleton Ni /PABA electrode can be used for the detection of dopamine (DA) in the concentration range 10^{-5} and 10^{-10} mol. L^{-1} in aqueous phosphate buffer solution at pH = 7.4. The slope of the calibration curves is higher for the PABA skeleton Ni electrodes, showing that a higher specific surface and a higher density of boronic groups, improves the sensory response.

The adsorption process of azo dye on electrochemically deposited PANI nanofibers on the Nb electrode is well described by the Langmuir model. The adsorption process occurs spontaneously, through both chemical and physical adsorption. Chemically prepared PANI added in the formulation of solid membranes for "dry" batteries (solid polymer electrolytes-SPE) avoids salt aggregation. As a result, the concentration of free ions increases by improving the dispersion of lithium salt in the membrane. The results obtained for the hydrogen evolution reaction (HER) show that the Ni/PANI electrode has a porosity and morphology capable of ensuring a superior contact between the substrate and the electrolyte solution. In hydrogen release, the porous structure is important, depends on the existence of bridging pores (the pores could be more or less regular in their geometry) and brings significant variations in the relaxation time constants. For the PANI films obtained at intermediate scanning speeds, the presence of granular inclusions in the nanofibrillar morphology further reduces the contacts between the PANI chains and, as a result, the films show higher values of resistance to charge transfer. The studies related to the synthesis, characterization and applications of conductive polymers presented in this thesis are the subject of 6 articles published in ISI journals, of which the candidate is the main author or co-author. Part of the results were obtained from a research project in partnership where the candidate was responsible for the project (PNCD II Contract No. 71-004/2007) and part in collaboration with the Polytechnic University of Timisoara.

Chapter 2 includes the research carried out in collaboration with the Crystal Engineering, Growth and Design Laboratory from the University of Heraklion, Crete. Subchapter 2.1 describes the importance and current state of research in the addressed research field. Corrosion studies have

focused in particular on inhibiting the corrosion of iron and its alloys. We used electrochemical techniques in the research carried out that aimed to study the properties of corrosion inhibitors offered by tetraphosphonic acids (subchapter 2.2.), diphosphonic acids subchapter (2.3) and polyester coatings with metal-organic framework with phosphorus (MOF) as potential inihitor (subchapter 2.2.). Corrosion currents vary for carbon steel immersed in saline solution depending on the nature of the inhibitor. Corrosion currents decrease in the presence of di and tetra phosphonic acids as a result of the generation of a well adsorbed inhibitor layer on the surface. The quality of the protective layer depends on the length of the alkyl chain, on the ability to pack and bind to the metal surface through P-O-Me bonds. Phosphonic acids behave as a mixed type inhibitor, by reducing both cathodic and anodic reactions. The addition of metal phosphonate in polyester polymer coatings improves the corrosion behavior of the film. The promising results obtained with the alkyd resin containing the Mg(GLY) additive suggest that this type of resin can be applied directly for iron protection without the need for a primer layer. This not only brings economic benefits, but also saves time.

Further research is recommended to investigate the long-term behavior and accelerated aging of these coatings under UV exposure. Understanding the mechanism of action of the investigated inhibitors was achieved by combining several techniques, such as infrared spectroscopy, XPS, impedance spectroscopy, optical microscopy. The studies related to this corrosion presented in the thesis are the subject of 3 articles published in ISI journals, of which the candidate is the main author or co-author.

Section II includes plans for career advancement and development. The main future research directions are intended to be a continuation of the current research themes. Therefore, my future research will focus on the following: the creation of new sensors, based on carbon or special polymers; investigation of the corrosive protection mechanism offered by natural and synthetic compounds to the metal substrates of interest. A new direction of research aims at environmental protection, reuse of waste in an intelligent manner, namely the recovery of fats from waste water from domestic and industrial waste and the use of recovered fatty acids in the production of marking paints or semi-conductors or colored polymer premixes.