HABILITATION THESIS

Processes and materials in electrochemical energy systems

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Abstract

The present habilitation thesis entitled "Processes and materials in electrochemical energy systems" is a synthesis of the research activities carried out by the candidate after obtaining the scientific title of Doctor in Chemical engineering in 2004. The main research directions are the electrocatalysis of hydrogen evolution reaction and the electrochemical synthesis of conducting polymer films and the study of charge transport mechanism within such films.

The thesis consists of two parts, the first part presenting the main scientific, professional and academic achievements, and the second part contains the plans for evolution and further development of the research and university career.

Part I of the thesis is divided into two sections, of which ***Section I*** presents the main scientific achievements in the research fields approached, based on the original results published in 14 selected ISI papers, and Section II presents the main professional and academic achievements between 2004 and present. These include the publication of 29 articles in ISI-indexed journals (*h*-index 11) and 2 books, 1 patent, 3 research projects as principal investigator, member in the research team of 10 research projects, from which 1 international project, and respectively member in the target group of 3 POSDRU projects. ***Section II*** briefly outlines the main professional and academic achievements after obtaining the title of Doctor. The professional development involved the advancement from the position of assistant to assistant professor in 2005, respectively associate professor in 2008. From this position I have won two grants for equipping and modernizing the laboratories of Electrochemistry and General Chemistry. I was also involved in 3 POSDRU projects: Development and implementation of master programs in micro- and nanomaterials, Increasing the attractiveness and performance of doctoral and post-doctoral training programs for researchers in engineering sciences and Doctoral School in support of research in European context, of which the last project was specifically devoted to potential doctoral advisors and contributed to my training as a future doctoral supervisor through active involvement in coordinating a doctoral student.

The main scientific achievements are presented, divided in 3 chapters corresponding to the main research directions approached, namely Contributions on the electrocatalysis of hydrogen evolution reaction, Contributions on the electrochemical synthesis of nanostructured polyaniline, respectively Contributions on the charge transport mechanism in conducting polymer films.

Chapter 1 presents a continuation of the research carried out during the PhD thesis, being one of the research directions initiated in the Laboratory for Electrochemistry, Corrosion and Electrochemical Engineering, which led to the elaboration of 2 PhD theses and the publication of 4 articles in ISI ranked journals, to which the candidate is a co-author. The investigations aimed at accelerating the hydrogen evolution reaction by using electrocatalysts added in the solution. These catalysts, also called proton carriers, have the ability to increase the proton concentration in the double electric layer from the metal-solution interface by transporting the protons from the bulk of the solution to the interface. The results obtained have shown that the catalytic effect of the proton carriers is manifested for both electrode materials with high hydrogen overpotential, such as copper, but, more important from a practical point of view, even in the case of metals with low hydrogen overpotential, namely gold and platinum. Various aromatic or aliphatic amines were investigated as proton carriers, since the ability to carry protons is given by the lone pair of electrons of the nitrogen atom. The results obtained showed that the catalytic effect of the amines on the hydrogen evolution reaction can be explained based on their molecular parameters obtained by modeling, the most important being the dipole moment and the surface coverage degree. Thus, the most pronounced catalytic effect was obtained in the case of amines with a low surface coverage, which is equivalent to a larger number of molecules present at the interface, so an increased proton concentration, and respectively for a large dipole moment, which indicates a favorable orientation of the molecules at the interface, namely with the nitrogen atom and the attached proton directed towards the metal, where the charge transfer is greatly facilitated.

Chapter 2 describes one of the research directions initiated by the candidate in collaboration with the Institute of Chemistry of the Romanian Academy, which led to the elaboration of one PhD thesis and 5 articles in ISI ranked journals where the candidate is the principal author or co-author, part of the results being obtained within the framework of a Partnership research project coordinated by the candidate as partner responsible. The aim of the research was to investigate the influence of working conditions on the electrochemical synthesis of nanostructured polyaniline, namely the influence of acid concentration and the monomer / acid molar ratio, as well as the influence of scan rate, temperature and substrate. The results obtained have shown that polyaniline nanofibers can be obtained by electrochemical synthesis on different electrode materials under specific conditions of each substrate. It has been also found that capacitance values, which indicate the ability of polyaniline films to store electrical charges, are much higher for nanostructured polyaniline films as compared to those with granular structure. It has been also demonstrated the use of conductive polymer films in various applications, such as the development of dopamine biosensors and the adsorption of azo-dye pollutants.

Chapter 3 refers to the results obtained in collaboration with the Center of Spectroelectrochemistry of the Leibniz Institute of Solid State and Materials Research in Dresden, Germany, during 5 post-doctoral research stages and subject to 5 papers published in ISI indexed journals to which the candidate is the main author or co-author. The researches carried out have studied the charge transport mechanism in conductive polymer films such as polyaniline and polythiophene. For this purpose, spectroelectrochemical methods were used *in situ*, which allow the simultaneous recording of spectra during a cyclic voltammogram, which is equivalent to the real-time generation of spectra for various intermediates resulting from the electrochemical oxidation of conductive polymers. The combined application of several such techniques, such as infrared spectroscopy, electron spin resonance spectroscopy, and ultraviolet and visible spectroscopy, allows the differentiation of paramagnetic and diamagnetic species and the unambiguous assignment of adsorption bands to various charge carriers, such as polarons, bipolarons or polaron pairs. The results obtained have shown that in the case of polyaniline phenazine-like structures play an important role in the formation and stabilization of the charge carriers. In the case of substituted polythiophene derivatives, it has been shown that polarons and polaron pairs are the main charge carriers at low doping levels, respectively, bipolarons and polaron pairs at high doping levels.

Part II of the habilitation thesis includes plans for career evolution and development. The main future research directions are presented as a continuation of the actual research interest. Thus, based on the research and expertise in electrocatalysis of hydrogen evolution reaction, our research group is partner in a HORIZON 2020 proposal submitted in 2017: *Novel modular stack design for high pressure PEM water electrolyzer technology with wide operation range and reduced cost* – **PRETZEL**. The trends in my future research work will be focused on: (i) development of new electrocatalysts for hydrogen evolution reaction; (ii) development of new biosensors using carbon based materials such as conducting polymers and carbon nanotubes and (iii) development of supercapacitors for electrochemical energy storage using conducting polymers.