ABSTRACT

In this habilitation thesis that represents a sum of more than 25 ISI-ranked papers as principal author and about 7 PhD thesis for which the candidate activated as daily PhD supervisor, Florica MANEA’s research activity is briefly presented and structured based on the research themes and chronological evolution.

The first part consisted of the main research activity already performed linked to the published results. Graphite-based composite electrode materials for the electroanalysis, graphite-epoxy composite microelectrode for biosensing, nanostructured-carbon composite electrode materials for electroanalysis and advanced water treatment using electrochemical, photocatalysis-assisted electrochemical and photoelectrocatalytical processes are the main research themes initiated and developed by the candidate after PhD completing and defending.

The results presented in Graphite-based composite electrode materials for the electroanalysis were obtained mainly in the framework of a CEEX-ET Romanian excellence research project developed and managed in the period of 2005-2007 by the candidate. In this period, our research group performed the design and the manufacture of special unmodified/zeolite modified-graphite-based composite electrode material for the electroanalysis application envisaging in principal the detection of the organic pollutants from water. Also, the specific advanced electrochemical techniques were optimized for these certain compositions to achieve high electroanalytical performance. Various electrodetection schemes and protocols involving specific electrochemical techniques were proposed in direct relation to the target analyte (pollutant). Linear-scan voltammetry (LSV), cyclic voltammetry (CV), chronoamperometry (CA), differential-pulsed voltammetry (DPV), square-wave voltammetry (SWV), and multiple-pulsed voltammetry (MPA) have been employed for the electrode characterization and application in the electrodetection. Selected organic molecules were chosen to represent target pollutants in aqueous solutions, i.e., phenol derivates as priority organic pollutant (POP), thiourea (TU) for sulfur-based impurities, glucose (GL) for carbohydrates, and urea (UR) for nitrogen-based impurities. In principal, the detection schemes for the individual determination of the target analyte were developed and in addition, the simultaneous detection related to the specific application were tested and discussed. The results were disseminated by published papers and 1 PhD thesis.

Graphite-epoxy composite microelectrode for biosensing represents an approach that considered the properties of the graphite composite macroelectrode and its miniaturization possibility to be able to use it for in-vivo detection of dopamine (DA) and molecular O_2 at the brain level. This study was developed by cooperation with the University of Sassary, Italy with the main idea to find an easy method to construct a graphite-composite microsensor suitable for the implantation in brain. Certain graphite-based composite microsensors were proposed for the selective electrochemical detection of DA in the presence of ascorbic acid and for in-vivo O_2.
detection in brain. Besides published papers, these results have been disseminated also as PhD thesis.

In the framework of Romanian exploratory research project PNII Ideas 165/2011, our research group has been investigated the synthesis, characterization and application of the unmodified/modified nanostructured carbon composite electrode in the electroanalysis, in order to improve the electrodetection performance. Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as nanostructured carbon were used also as substrate for the electrodeposition of metallic nanoparticles, Ag and Cu. Zeolite-modified and metal organic framework (MOF)-modified nanostructured carbon composite electrode were prepared and tested for certain electroanalysis applications. In addition, based on the good photo(electro)catalytic properties of titanium dioxide (TiO$_2$) and combining the superior characteristics of TiO$_2$ and CNTs, the TiO$_2$-modified nanostructured carbon composite materials was tested for the detection of phenol derivates. The electrochemical detection performance is directly linked to the electrochemical properties of electrode surface in conjunction with the specific electrochemical techniques. Various compositions for nanostructured carbon based composite electrode were synthesised, characterized and applied for the electroanalysis of various target analytes ranged from water pollutants, to pharmaceuticals and biological molecules. An exhaustive study was investigated for POPs detection and the superiority of these materials was proved in comparison with above-presented graphite-based composite electrodes. Also, specific detection protocols were elaborated for pharmaceutical, i.e., ibuprofen (IBP), diclofenac (DCF), fluoxetine (FLX). The stripping anodic voltammetry based electrochemical detection was elaborated for individual arsenic detection, method that was patented, and modified for the simultaneous detection of arsenic and lead from water. Very interesting and useful aspects for electroanalysis linked to electrochemical behaviours were discussed. Taking into consideration the main advantage of the composite electrode due to the specific behavior of ensemble/array of microelectrodes, the electrochemical detection schemes for in-field electroanalysis were elaborated. Two PhD thesis were elaborated based on these results.

In Advanced water treatment using electrochemical, photocatalysis-assisted electrochemical and photoelectrocatalytical processes, three types of advanced oxidation processes (AOPs) have been developed in our group based on the electrochemical oxidation, i.e., photocatalitically-assisted electrooxidation and photoelectrocatalysis. Designing the electrochemical process for the advanced treatment of the various pollutants-containing wastewater using carbon-based electrodes has been investigated. Phenol derivates, dyes, pharmaceuticals were selected as model pollutants for wastewater treatment and natural organic matters for water treatment. Carbon-based composite electrodes were studied in comparison with commercial glassy-carbon (GC) and boron-doped diamond (BDD) in order to select the best electrode for application in the AOP processes. BDD-based electrooxidation process has been investigated to integrate it within drinking water treatment technology to destroy natural organic

Florica MANEA
matter. This study represents a part of research activity of a Romanian collaborative project WATUSER 60/2012. Two approaches have been considered to reach the main aim of the study regarding advanced electrooxidation process, one is refer to the determination of the electrochemical performance of the electrode material for the degradation/mineralization using cronoamperometry (CA) and multiple-pulsed amperometry (MPA) techniques and the second one envisaged the determination of the process efficiency under optimum operation conditions by bulk electrolysis (electrode material, pH, current density, pollutant concentration range). In order to improve the performance of the advanced electrooxidation process taking into account the technical-economic criteria (reduced energy consumption), two types of the electrochemical involved process have been studied, the photocatalytically-assisted electrochemical and photoelectrochemical processes. Both processes is based on TiO₂ photocatalyst integration within the electrochemical oxidation process, one as suspension form and the second within the electrode composition. In addition, these studies envisaged testing dual character of the electrode material and the electrochemical techniques both for advanced degradation of some pollutants and the degradation process control by specific detection schemes, and these preliminary results are very promising. Three PhD thesis were elaborated based on these results.

The second part consisted of the future research activity that will be focused on:

i. new and advanced electrode materials characterized by the enhanced properties in relation with sensing applications;

ii. new and advanced electrode materials characterized by the enhanced properties for energy storage;

iii. developing new electrochemically-based advanced processes for water/wastewater treatment technology at pilot-scale;

In addition, in the framework of the Romanian-Swiss collaborative Program new research field was opened regarding the new tools for environmental management, e.g., environmental impact assessment, environmental risk assessment, eco-efficiency, which will be further developed.