

UNIVERSITY "POLITEHNICA" BUCHAREST
FACULTY OF MATERIAL SCIENCE AND ENGINEERING

PhD THESIS

STUDIES AND RESEARCHES CONCERNING THE INFLUENCE OF DOPING
AGENTS ON THERMAL PROPERTIES OF COMPLEX NANOSTRUCTURED
OXIDES WITH APPLICATIONS FOR ENVIRONMENT AND GREEN ENERGY



Summary

PhD student:

Eng. Ioan Albert TUDOR

Scientific coordinator:

Prof. Dr. Eng. Cristian PREDESCU

2017

Contents

INTRODUCTION.....	3
Chapter 1. International state of the art in respect with the most recent literature references...	3
Chapter 2. Theoretical contributions regarding the methods of obtaining and functioning the complex oxide materials for environment and green energy	4
Chapter 3. The research methodology and analysis techniques used to achieve the objectives of the thesis	5
Chapter 4. Researches on interactions at the interface carbon substrate -ZnO coatings	6
Chapter 5. Researches regarding the preparation and characterization of the carbon foams	6
ZnO nanoparticles attachment to the inner surface of the carbon foams. Experimental procedure.....	6
Chemical and structural characterisation of the carbon foams	7
Grain size distribution and zeta potential of the precursor powders	8
Initial carbon foams characterisation.....	8
Characterisation of the ZnO impregnated carbon foams	9
Study of particle size and zeta potential for colloidal precursors of zinc hydroxi carbonate formed during hydrothermal impregnation of carbon foams.....	13
Mechanism of ZnO attachment to the carbon surface	15
Chapter 6. The fictionalization of the carbon foam surface with nanoparticles	21
Improving the thermal conductivity of M.A.S.A.	21
Chapter 7. General conclusions. Original contributions. Research directions	35
General conclusions.....	35
Original contributions	37
Research Directions	37
References - selection	38

INTRODUCTION

The scope of this thesis is to improve and develop new phase change materials (PCM) for applications in seasonal storage of thermal energy in the range of medium temperature. These new materials are important because they can address both the commercial and residential buildings to heat their space in winter, using the energy collected by the thermal collector systems during summer, thus helping to better protect the environment. The importance and the derived concepts will be presented in following chapters.

The research theme proposed in this thesis has the objectives presented hereafter:

- To improve and develop new phase change materials for applications in seasonal storage of green energy at medium temperature.
- To study a series of experimental solutions to increase the thermal energy storage capacity by using PCMs based on sugar alcohols and approaching some methods that allow a controlled increasing of the exchange surface together with controlling the crystallization process during undercooling.
- To elaborate a simple process for hydrothermal impregnation which assures the functionalization of carbon foams with nanostructured ZnO with flowerlike morphology, which in turn will help to avoid the crystallization of the sugar alcohols selected as PCMs (Mannitol, Erythritol, Xylitol), during the thermal cycles that take place in the thermal storage system.
- To study the functioning mechanism of the carbon materials impregnated with ZnO particles to control the surface properties at the substrate/PCM interface.
- To study the thermal stability of the obtained composite system, using thermal analysis methods.

Chapter 1. International state of the art in respect with the most recent literature references

In this chapter there are presented the main requirements for the phase change materials based on molecular alloys of sugar alcohols, their classification, the way to improve the heat transfer to the PCMs, the way to increase the area of the specific exchange surface - the encapsulation of molecular alloys based on sugar alcohols (MASA).

The chapter begins with a description of the basic requirements of a material that can be used as a phase change material. Usually a single material is unable to meet the all these requirements and therefore an alloy is required.

The temperature of the phase transformation and the higher melting enthalpy represent two of the most important requirements that a PCM must fulfill. These materials must achieve their scope namely to store and to release heat. The main requirements can be grouped in three distinct categories: physical, technical and economical.

Sugar alcohols are relatively new materials thus there is little general information available about them. Their melting temperature is in the range 90-200°C, and their mass specific fusion enthalpy is relatively high for most of them. In addition, their density is also high, which also means very high volume specific fusion enthalpies. Compared with some other organic materials, sugar alcohols have stable subcooling. They are not harmful for the environment. The most usual sugar alcohols of natural origin, which are extensively used in food industry, are the following: Manitol, Erythritol, Xylitol, Sorbitol, Galactitol (Dulcitol). The most frequent sweeteners used instead of sugar are Erythritol and Xilitol.

The increase of the sugar alcohols thermal conductivity is possible by encapsulating them in an inorganic or hybrid matrix. The encapsulation will increase their exchange surface required for a good heat transfer when are used inside some porous carbon structures. These structures are also specially designed for a large surface area by nanoparticles embedding.

In the case of molecular alloys it is easy to adjust the melting point which usually leads to a significant increase of the energy density. What is more the eutectic alloys have melting points lower than those of the individual components.

Sugar alcohols based molecular alloys have the following advantages: low cost, ecological storage materials (non-toxic, non-corrosive), long term storage significantly reduces the thermal losses, easy to adjust the melting point in the range 70 - 180°C, expected energy density $>200\text{kWh/m}^3$, storing the heat released at high temperatures with the decreasing of the necessary power.

Unlike short term storage, the seasonal storage needs lower discharging power compared to the storage volume. The development of carbon foams aims to get to an equilibrium between cost, macroscopic thermal conductivity and the energy density of the final material (host + sugar alcohols based molecular alloys).

The synthesis of the porous structure can be done by using various hard or soft shapes and also various carbon precursors (e.g. sugars, alcohol etc.). The model is cheap due to the large variety of cheap precursors. In the same time, the fabricated structures meet the application requirements for seasonal storage of green energy: thermal conductivity and porosity including pore connection.

Chapter 2. Theoretical contributions regarding the methods of obtaining and functioning the complex oxide materials for environment and green energy

This chapter presents the hydrothermal synthesis of nanostructured ceramic powders, the applications of hydrothermal processes in the synthesis ultradispersed nanostructured ceramic powder, the mechanism, the thermodynamics and the kinetics of hydrothermal reactions, the factors that influence the hydrothermal synthesis of the nanostructured ceramic powders, the basic synthetic methodologies and methods for carbon substrate functioning.

Due to their chemical stability, electronic conductivity, ability to intercalate active electrochemical species and of course due to their sorption capacity, the nanostructured carbides are interesting materials for a number of energy storage applications.

Advantages can also be achieved by changing the carbon wall or surface composition. In this section highlights the applications of advanced mesoporous and macroporous carbon materials with a special emphasis on carbon functionalization effects on each application. While enormous advances have been made in the synthesis of advanced porous carbon materials with new morphologies, interesting challenges remain in the field of the functionalization of these materials and also in the field of the optimization of their properties for specific applications. The addition of surface groups allows the modification of the pore texture, wetting and surface reactivation. Pore wetting, surface hydrophobicity and hydrophilicity, all depend on the type of functional groups present on the surface and on the better reactant penetration into the pore system. As synthesized carbon materials produced by high temperature carbonization are hydrophobic and suitable for the acquisition of components in oil, aromatic substances and other non-polar systems. Superhydrophobic properties can be achieved by fluorination.

The surface oxidation, the sulphonation or the introduction of other charged groups make pore surfaces more accessible for polar fluids.

In terms of the surface reactivity, its ability to establish carboxyl groups, para-functionalized benzene groups and reactive double bonds on its surface, the porous carbon structure provides anchoring points for various organic groups. At present electrochemical functioning seems to be the optimal method.

The number of functionalization methods that have been applied to advanced porous carbon materials is increasing. It can become significant if it is helped by the field of organic chemistry synthesis. It is desirable a better control over the density, stability and specific surface location of the functional groups. In mesoporous silicates, the incorporation of several

functional groups has been found to be more advantageous for some systems and similar approaches have been used for porous carbides.

The heating conditions have a great influence on the pore structure and on the performance of the carbon foam. A carbon foam with larger pores has higher porosity, lower density, much better compressive strength and more interconnected pores.

When functional groups are not directly included during the synthesis of porous carbon materials, controlled oxidation can be used to introduce oxygen-containing groups on the carbon surface and sample preparation for subsequent modifications through covalent, electrostatic interactions in the hydrogen bonds. Controlled oxidation improves the wettability of pores in respect with the polar solvents, increases the proportion of micro poros and the carbon surface. The modification of the sample texture can be achieved by activating carbon with KOH or CO₂.

Porous carbon materials functionalized with sulfuric acid groups have been investigated as potential environment-friendly acid-based catalysts. Functionalized carbon eliminates the need for liquid acids in certain catalytic reactions and can be reused several times.

Surface modification can drastically change the physical properties of carbonaceous materials. Fluorination is used to create a hydrophobic carbon surface.

Chapter 3. The research methodology and analysis techniques used to achieve the objectives of the thesis

This chapter presents the hydrothermal synthesis and the in-situ attachment of ZnO colloidal nanoparticles within the porous carbon structures, the influence of temperature and pressure on the solution reaction rate, the analysis methods used to investigate the complex oxide systems intended for applications in the field of environment and green energy: thermal methods, FT-IR, XRD, imaging methods, laboratory technological flow-sheet.

The carbon foams were functionalized by impregnating them with nanostructured ZnO particles with "flower-like" morphology. In this way, interference interactions with sugar alcohols can be controlled, taking into account the phase change of the materials for the development of thermal energy storage applications. Functionalization of carbon surfaces is necessary to reduce as much as possible the probability of heterogeneous nucleation.

The methods to develop functionalized carbon surfaces via the incorporation of a secondary phase within the carbon frames are classified into three major groups: impregnation, metal transfer reactions and composite foams. The impregnation methods are widely used because they are easier to make and less costly for metal oxides.

The proposed hydrothermal method is advantageous because it involves the homogeneous nucleation in a single step at moderate temperatures and pressures without subsequent heat treatment in a closed vessel.

The development of modern techniques suitable to analyse materials at nanoscale has helped to increase interest in nanotechnology at industrial level.

Thermal Analysis (ATD) and Differential Calorimetry (DSC) record the temperature variation of a sample when the furnace temperature is constantly increased and compared to a thermally inert (Al₂O₃) standard sample. The temperature difference is controlled by a differential thermocouple system. Thermal changes accompanied by mass variation are studied by thermogravimetric (TG) methods. Thermogravimetric analysis records the weight variation of a sample as function of temperature.

FT-IR spectroscopy has been used to determine functional groups existent on coal, activated carbon structures, and is also suitable for investigating advanced porous carbon materials. In order to evaluate the success of surface functionalization, it is advisable to compare spectra recorded before and after treatment and to monitor the appearance and disappearance of absorption bands.

To determine mesostructural periodicity, pore geometry and cell unit parameters of mesoporous carbon advanced materials, the most useful technique is based on X-ray diffraction. The imaging of functional groups in porous carbon samples was performed by scanning electron microscopy (SEM).

Chapter 4. Researches on interactions at the interface carbon substrate -ZnO coatings

Impregnation methods are widely used because they are relatively inexpensive and easy to carry out. Metal oxides and mixed oxides are formed inside the mesopores of a carbon substrate after a series of steps including wet impregnation, drying and calcination.

In the case of the present research, the solution chosen to meet the technological conditions and to obtain ZnO films with controlled thickness only on the inner surface of the pores, involved the use of urea as agent for Zn^{2+} homogeneous nucleation on the carbon surface.

For the estimation of the synthesis parameters need to deposit ZnO films on the carbon pore surface, the first step consisted in the thermodynamic evaluation of Zn-H₂O-CO(NH₂)₂ system using the HSC software.

The in-situ synthesis and the fixation of nanoparticles in the pores of carbon foams has been performed by the hydrothermal method due to the excellent solvent properties of water (virtually all metals can be dissolved by forming hydrate species).

The optimal reaction conditions of the studied systems (pressure, temperature, pH) can be established by means of thermodynamic calculations. It is possible to analyze the effect of different variables on chemical systems at equilibrium by simulating real working conditions.

Most researches on the hydrothermal synthesis process are based on the intelligent modeling of hydrothermal reactions carried out before the actual experiments begin. This modeling is particularly useful for predicting the experimental conditions to obtain the desired phase with controlled size and shape.

The equilibrium constant of the hydrolysis reaction increases with increasing temperature, which shows the advantages of the hydrothermal process on the reaction yield.

Under hydrothermal conditions at 200°C, the major solid species expected to precipitate inside the macroporous carbon is Zn₅(OH)(CO₃)₂ zinc hydroxycarbonate, over the entire pH range.

According to the thermal prediction, at temperatures above 200°C the zinc hydroxycarbonate is totally converted to ZnO.

Chapter 5. Researches regarding the preparation and characterization of the carbon foams

ZnO nanoparticles attachment to the inner surface of the carbon foams.

Experimental procedure

The surface of the carbon foams selected samples was treated by boiling them in 1M nitric acid solution for 1 hour in order to create an additional surface layer of functional groups that in turn will enhance the reactive adhesion of the ZnO nanoparticles.

After weighing the corresponding amount of Zn(NO₃)₂*4H₂O was dissolved in distilled water to prepare a 0.1M solution of zinc nitrate. Urea powder of analytical purity was also used to prepare a 0.2M aqueous solution. These two solutions were then mixed by electromagnetic stirring.

The carbon foam samples previously treated in nitric acid were placed in a vertical autoclave. Then the Teflon vessel was filled with a stoichiometric mixture of the two solutions of urea and Zn(II). After sealing the autoclave the immersed samples were hydrothermally treated for 2h at the maximum temperature of 250°C and autogenous pressure (due to the atmosphere above the solution). After finishing the experimental programme the samples were

removed from the autoclave and cut in several pieces intended for the necessary chemical, structural and thermal characterization.

The Teflon vessel was rinsed with distilled water to collect the white precipitate of hydrated zinc hydroxyl carbonate. After 3 steps of distilled water washing and filtering the powder was subjected to chemical, XRD and DSC-TG characterization. Both the impregnated samples and the collected powder were thermally treated in a digital chamber electric furnace for 2h at 500°C.

The methods for fictionalization of the porous carbon structures are based on: the direct incorporation heteroatoms during synthesis, oxidation and surface activation, halogenation, sulfonation, attachment of nanoparticles and deposition of surface films consisting of certain polymers.

In respect to the present state of the art, this thesis proposes an innovative single step method which assures the in-situ synthesis and the attachment of the nanoparticles inside the pores of carbon foams, by using the hydrothermal procedure, with the following advantages: low synthesis temperature, morphology control, homogenous nucleation, low environmental impact. Based on the thermodynamic prediction studies performed at INCDMNR-IMNR, there was proposed a method based on the hydrothermal-electrochemical deposition of ZnO which nucleates inside the macro-pores due to the reaction of Zn²⁺ cations with urea. The studies and the experiments subsequently performed have shown that the nanoparticles attachment can be done at the same synthesis parameters without an external electric field.

Table 1 briefly presents the working parameters, the monitoring methods and the necessary characterisations.

Table 1. Conditions for graphite foam impregnation (laboratory scale) with ZnO

Parameters	Interval	Equipment and Monitoring
Temperature of hydrothermal treatment, °C	200-225	Vertical autoclave, water cooled system, T and P sensors, computer controlled
Pressure, bars	50-75	
pH range	8-10	Digital pH-meter
Zn concentration, Mol/L	0.1-0.3	Chemical analysis (ICP, AAS)
Urea concentration	Stoichiometric	Gravimetry
Temperature of thermal treatment, °C	350-400	Digital furnace

Chemical and structural characterisation of the carbon foams

The parallelepiped samples of carbon foams, whose dimensions were accurately measured with an electronic baffle, were first weighed, and the corresponding bulk density, ρ_b , of the blocks was simply calculated as the ratio between mass and volume. Several samples were finely grinded in an agate mortar, and the resulting powder was analysed with a helium pyrometer to obtain the skeletal density, ρ_s . The total porosity, Φ , was calculated with the following relation: $\Phi = 1 - \rho_b / \rho_s$. The samples microstructure was analysed by optical microscopy.

The thermal conductivity was measured by the transient plane source technique with a ThermoConcept Hot Disk TPS 2500 equipment.

Zinc content in the precipitated powder and in carbon foams was measured by direct plasma coupled spectroscopy (DCP-Spectroflame) according to ASTM E 1097/1993, and the calcination losses of the precipitated powders were determined according to the standard SR ISO 60606- 2000.

The DRX structural characterization was performed on a BRUKER D8 ADVANCE diffractometer using the Bragg-Brentano diffraction method. Data acquisition and processing was performed using the DIFFRACplus BASIC Evaluation Package, the EVA 12 Release 2006 (Bruker AXS) and the ICDD PDF-2 with the Release 2006 database.

Optical microscopy was performed using a Zeiss AXIOMAGER A1m microscope. The same samples were used to analyse the morphology of the ZnO nanoparticles attached to the carbon surface by SEM using a HITACHI S2600N system.

The thermal characterization of carbon foams before and after the addition of ZnO and precipitated powders was done by differential scanning calorimetry and thermogravimetry (DSC-TG) using a SETARAM Setsys equipment. The measurements were performed from room temperature up to 1600°C.

Grain size distribution and zeta potential of the precursor powders

Particles size and their surface zeta potential were analysed by dynamic light scattering with a Zetasizer ZS90 (Malvern Instruments Ltd) device equipped with an automatic titration system. The particles were sonicated for 3 hours in a 10⁻³ M NaCl solution, pure or with the addition of polyacrylic acid sodium salt (PAAS, molecular weight 25000) and polyethyleneimine (PEI, molecular weight 1200) as a dispersing agent. The total volume of the sample was kept constant at 100 ml. The weight ratio of PAAS and PEI was kept constant at 10⁻³ mg for 1 g of dispersed powder. The influence of pH was studied by self-titration with HNO₃ and NaOH using three different concentrations (0.2 M, 0.3 M and 0.5 M).

Initial carbon foams characterisation

Archimedes method was used for porosity evaluation:

$$\text{Open porosity} = \frac{(\text{mass of sample after boiling in water} - \text{initial mass}) \cdot 100}{\rho_{\text{solvent}} \cdot \text{sample volume}}$$

Note: water is not the best solvent due to the small differences between densities – some samples have floated.

Two types of carbon foams prepared at CNRS, France were used. They were denoted L1 and C1. The results for the open porosity are presented below:

$$p(L1) = 47,8 \dots 62,3 \%$$

$$p(C1) = 61,90 \dots 64,45 \%$$

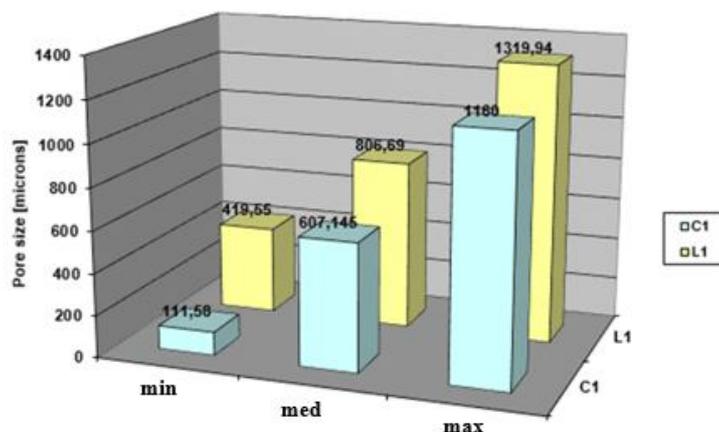


Figure 5.1. Pore size estimated from the micrograph analysis obtained with the AxioImager A1m polarized light microscope (Zeiss, Germany)

The microscopic study shows that both L1 and C1 samples are made up of graphite grains (grains more pronounced in the case of L1) and have a vacuole structure with open and closed pores.

X-ray diffraction was used to analyse the microstructure of carbon foams. The L1 sample consists (100%) of well-crystallized graphite, and the C1 sample presents a more complex phase composition. The C1 sample is a mixture of graphite with 1% quartz (SiO₂).

The influence of hydrothermal treatment on pore size distribution is shown in the following figures.

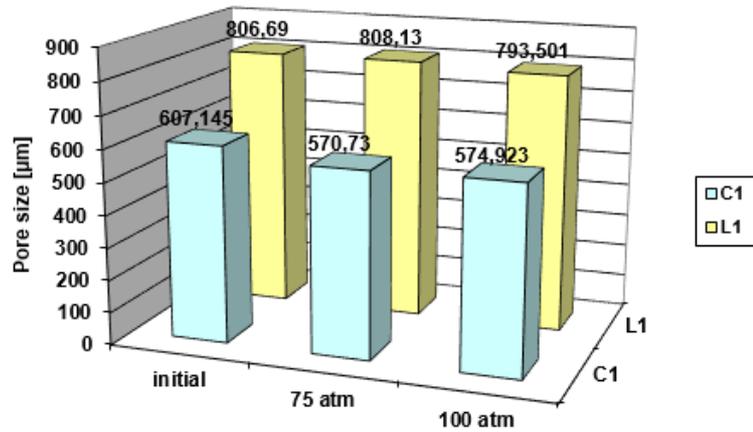


Figure 5.2. Evolution of the average pore size with increasing of pressure during hydrothermal treatment

The treatment at 100 atm pressure leads to an expansion of large pores and to a contraction of small pores, probably due to the light plastic behaviour of the structure. The maximum pore size of L1 increases with about 15%. Under the same conditions, the maximum pore size of C1 increases with 12.71%.

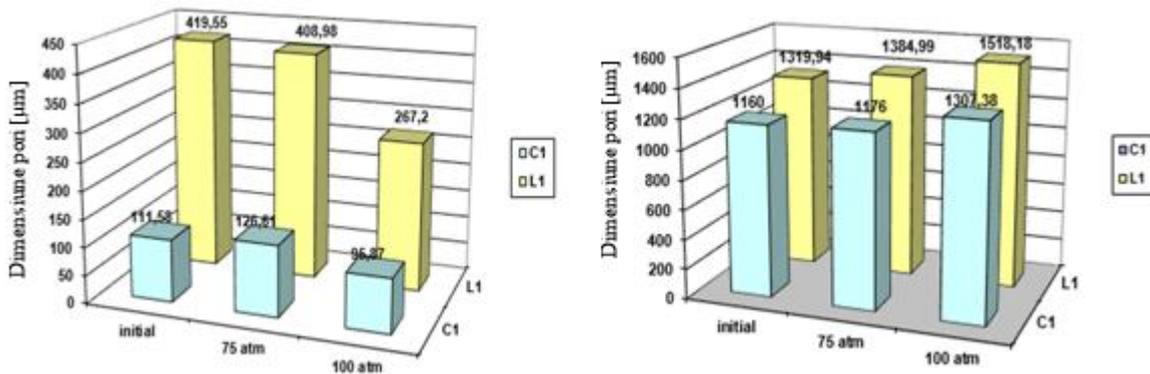


Figure 5.3. Evolution of the minimum and maximum pore sizes with increasing of pressure during hydrothermal treatment

The differences between the open porosity determined by the Archimedes method and the value calculated from the densities is important, about 15%.

Characterisation of the ZnO impregnated carbon foams

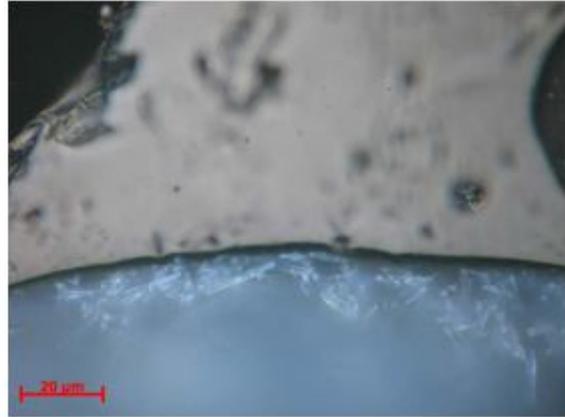
The two types of carbon foams were analysed on the optical microscope after being subjected to in-situ impregnation under hydrothermal conditions. The micrographs (reflected light, NII) show the presence on the surface of the samples of a coating with variable thickness (<10 µm), consisting of acicular shape crystals that make up a dendritic-like structure. Coatings are not compact.

The coating consists of a complex mixture of two different types of zinc hydroxide carbonates (hydrated and non-hydrated) and the zinc-β metastable hydroxide. The very high intensity of the peak at $2\theta = 13^\circ$ corresponds to a preferential increase.

After the heat treatment, the coating material completely crystallizes as zinc (ZnO), this being the only phase observed by DRX analysis.



Figure 5.4. Impregnated L1 sample



Impregnated C1 sample

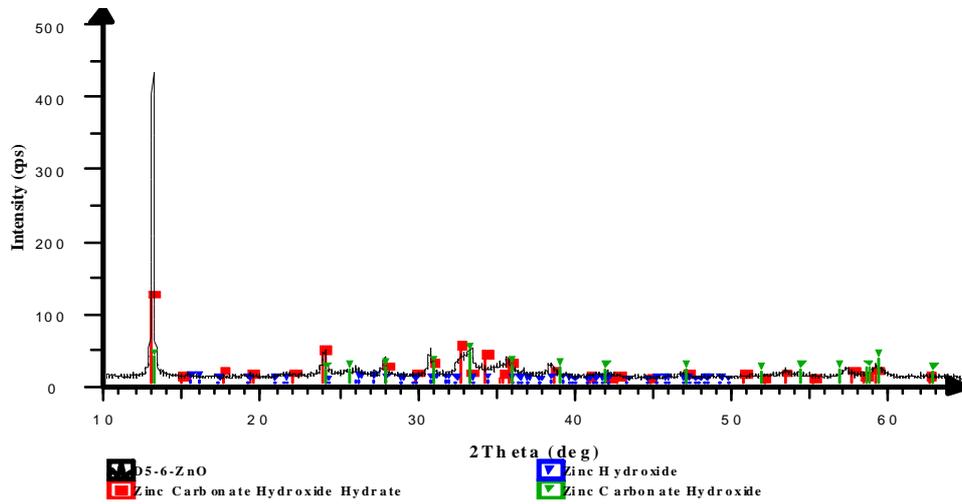


Figure 5.5. XRD spectrum of the coating material

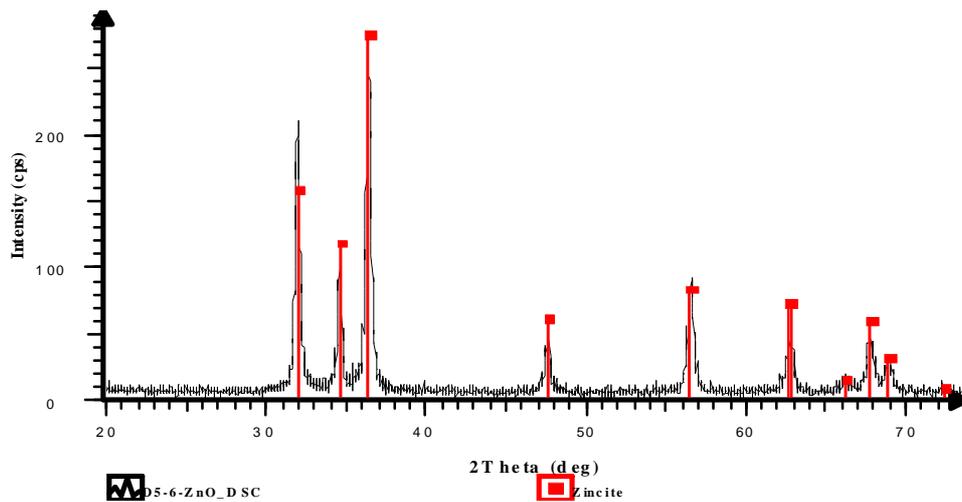


Figure 5.6. XRD spectrum of the coating material after heat treatment at 590°C in the DSC furnace, ZnO is the only identified phase

The XRD results are supported by the DSC analysis. The endothermic effect is due to the thermal decomposition of zinc hydroxi carbonate to zinc oxide (according to XRD and thermodynamic evaluation).

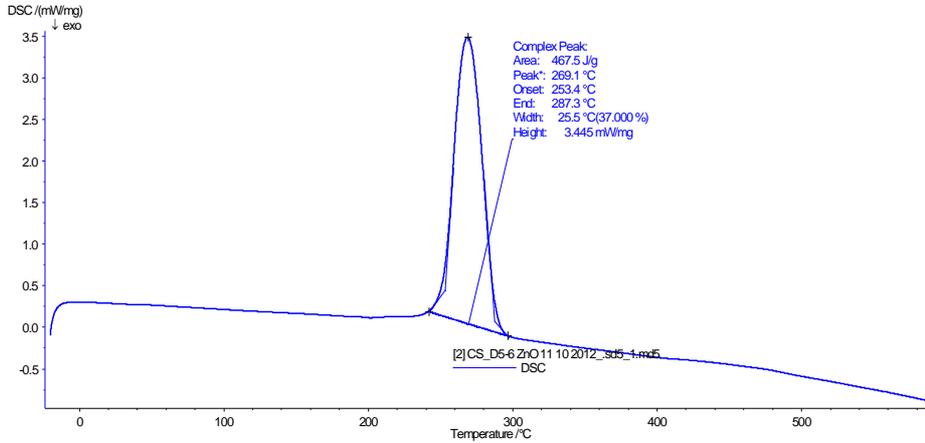


Figure 5.7. The DSC plot for the coating material

ZnO films were deposited on graphite membranes / plates by spraying:

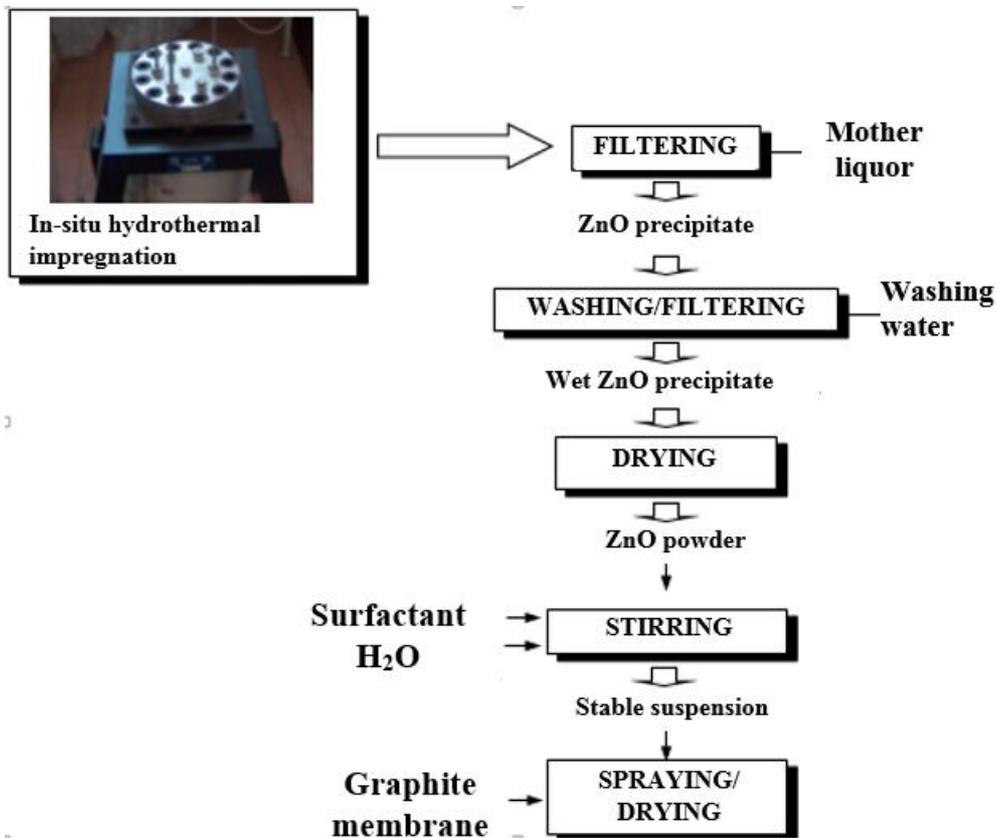
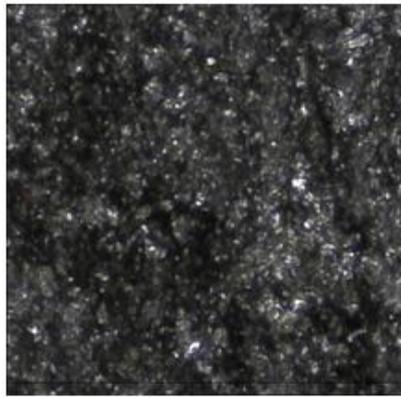


Figure 5.8. Spray deposition of ZnO films on graphite membranes/plates

The graphite structures used as substrate for ZnO films deposition by spraying, have a rough surface (as it can be seen in the micrograph below). The hardness tests were carried out with a NANOVEA M1 Scratch Tester, at loading pressures between 8 and 20N, leading to an average value of HV = 6.8366 (according to www.mindat.org the value for graphite is HV = 7-11).



Max Load(N): 1592.13
 Max Depth(μm): 231947.74
 Hardness(HV): 0.2440
 Hardness(HK): 4.2107
 Elastic Modulus(GPa): 0.1459
 Martens Hardness(GPa): 0.0113

 S (Indenter): 0.0500
 Indent: 42716.1
 m: 1.253
 S (Indenter): 0.0502
 Indent: 123849.36
 Area(μm²): 3.5954711

 Sample Name: Membrane Graph
 Load (N): 10.0000
 Loading Rate (N/sec): 32.0000
 Unloading Rate (N/sec): 32.0000
 Contact Load (mN): 10.0000

 Indenter Details
 Type: Berkovich
 Material:
 Radius (μm):

 Creep: 0 seconds
 Test Time: 10/02/12 11:01:00 AM

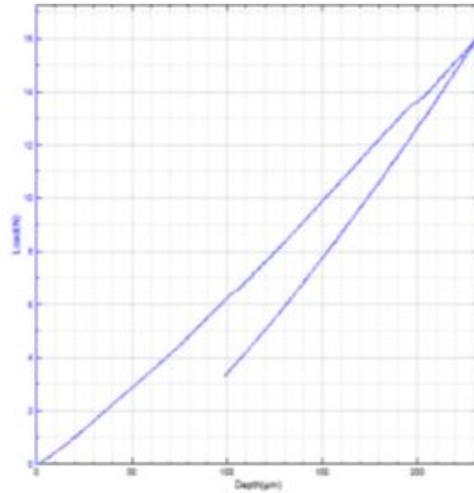


Figure 5.9. Graphite substrate

The graph Penetration depth / loading force – NANOVEA M1 Scratch Tester

The deposition obtained by spraying the suspensions of ZnO hydrothermal powders on the carbon substrates is a compact layer with variable thickness (between 10 and 20 μm). These films are made of isometric crystals, which can be seen in the micrograph below.

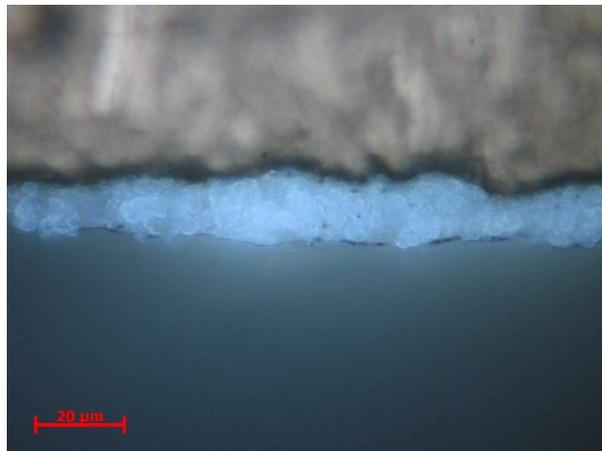


Figure 5.10. ZnO deposited by spraying onto graphite sample

The high degree of compaction of deposits is due to the narrow dimensional distribution of nanostructured hydrothermal powders of ZnO (see laser granulometry in Figure 5.11) –the particle size distribution is in the interval 110-356 nm, with an average particle size of 211.5 nm.

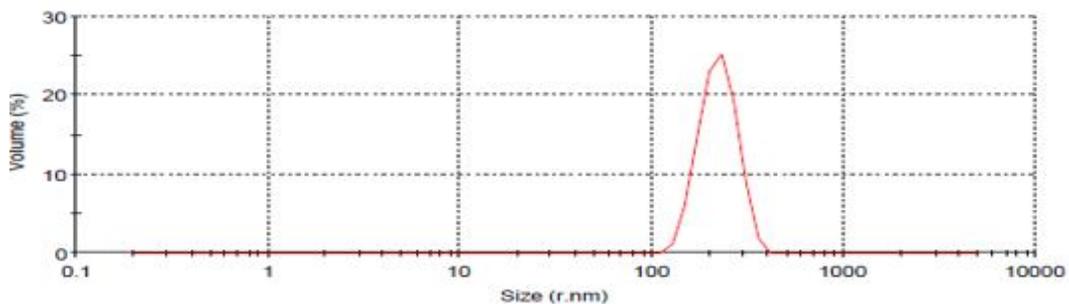


Figure 5.11. ZnO nanostructured powder – laser granulometry

The effective open porosity (about 60%) and the average pore size (> 600 microns) allow the in-situ hydrothermal deposition of thin ZnO films made of needle-shaped crystals.

The thermal treatment at $T > 300^{\circ}\text{C}$ is required for the decomposition of zinc hydroxi

carbonate to zinc oxide.

The stable ZnO suspension was successfully obtained directly from the hydrothermal process and was used to obtain compact coatings by spraying it with the help of compressed air.

It was observed a low yield for deposition inside the pores. To improve this yield two solutions were tested:

- The surface functionalization before hydrothermal reaction or the use of an organic solvent in the process;
- The use of very high pressure.

Study of particle size and zeta potential for colloidal precursors of zinc hydroxi carbonate formed during hydrothermal impregnation of carbon foams

Inside the pores, urea plays an important role in controlling the impregnation and adhesion of ZnO coatings with "flower-like" morphology to carbon surfaces. Table 2 shows the values of hydrodynamic diameters and zeta potential of dispersed zinc hydroxi carbonate hydrate at three different molar concentrations of 0.1M, 0.01M and 0.001M.

Table 2. The average values of the hydrodynamic diameters (dh) and of the zeta potential (ζ) corresponding to various conditions for water dispersion

Dispersion Concentration (M)	NaCl		NaCl+PAAS		NaCl+PEI	
	d_h (μm)	ζ (mV)	d_h (μm)	ζ (mV)	d_h (μm)	ζ (mV)
10^{-1}	3.774	36.6 ± 8.37	1.796	-94.8 ± 12.6	1.700	0.889
10^{-2}	5.967	-1.88	2.901	-119 ± 19.5	4.109	48
10^{-3}	2.518	-9.12	1.690	-101 ± 22.5	0.0987	11.6

Reports from the Malvern Zetasizer ZS90 equipment show good quality results for the average value of zeta potential, but the results for the hydrodynamic diameters are affected by the polydispersity of the sample, with the presence of large sediment particles.

The average dimensions of hydrated zinc hydroxide carbonate particles are significantly lower than the average cell dimensions of the carbon foams (approximately 800 μm) and their attachment inside the pores is feasible.

All the samples have a bimodal size distribution, except for the dispersion with 10^{-3}M concentration in the presence of PEI as a surfactant, which shows a trimodal distribution.

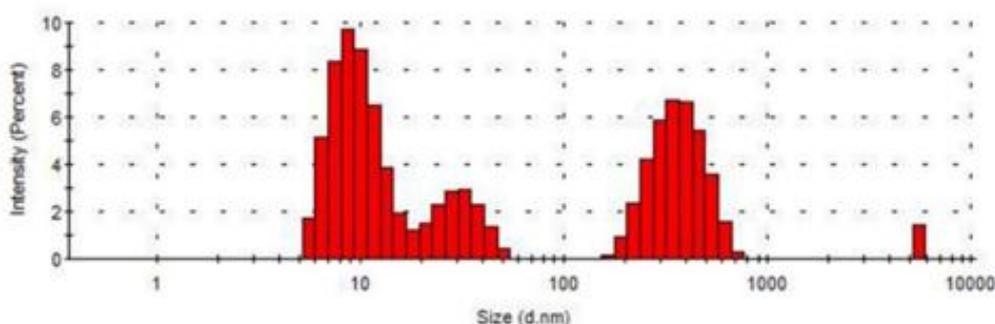


Figure 5.12. Histogram showing the particle size distribution of the 0.001M hydrated zinc hydroxi carbonate dispersed in NaCl solution

The evolution of the zeta potential of zinc hydroxide carbonate particles as function of the pH of dispersed solution at different concentrations is shown in Figures 5.13a-c.

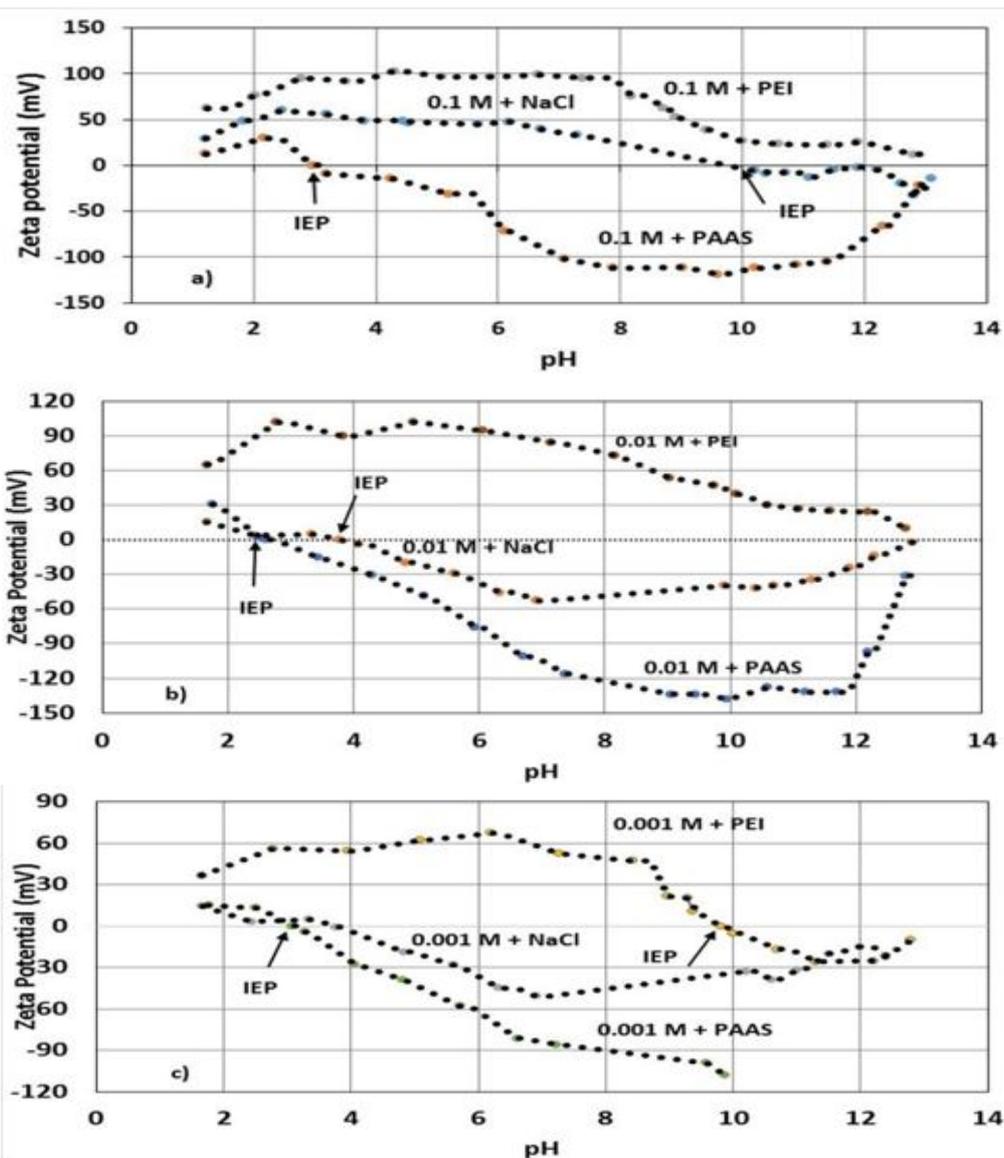


Figure 5.13. The evolution of zeta potential of zinc hydroxide carbonate dispersed in NaCl solutions and the effect of PAAS and PEI dispersants for the following particle concentrations:
a) 0.1 M; b) 0.01 M and c) 0.001 M

Particles dispersed up to a 0.1M concentration in NaCl solutions have a positive zeta potential in the pH range of 1 - 10, where a first isoelectric point (IEP) is observed. Decreasing the dispersion concentration to 10^{-2} M and 10^{-3} M, shifts the isoelectric point to acid pH (3.8 and 3, respectively). The addition of PAAS moves the isoelectric point to the acidic pH values for the dispersed particle concentration as follows: 2.96 for 0.1M; 2.61 for 0.01M and 3.08 for 0.001M. In the presence of PEI, suspensions with particle concentrations of 0.1 M and 0.01 M showed positive zeta potential for the entire pH range, as the isoelectric point was observed at pH = 9.8 for the particles dispersed at 0.001M concentration.

In the alkaline pH produced by the decomposition of urea in hydrothermal solutions, the decrease in the suspension concentration of the hydrated zinc hydroxide carbonate particles leads to a higher negative zeta potential and higher surface charges. The addition of PAAS increases the negative values of zeta potential, and the addition of PEI induces positive values of the zeta potential. These results show that hydrated zinc hydroxide carbonate particles formed during in-situ hydrothermal reactions between Zn (II) precursor and urea have negative surface charges, indicating the presence of hydroxylated zinc species such as $\text{Zn}(\text{OH})_4^{2-}$ on the

tetrahedral surface of the crystal. The electrostatic interactions between the surface charges of zinc hydroxide (ZCHH) carbonate particles and the dispersants can occur according to figure 5.14.

Therefore, the attachment of ZnO particles to the internal surfaces of porous carbon foams can be explained by the interactions between the partial negative charges of hydrated zinc hydroxide carbonate crystals and the positive ones belonging to the inner surfaces of the porous carbon structure, charges provided by additives, impurities and surface treatment performed before the hydrothermal treatment.

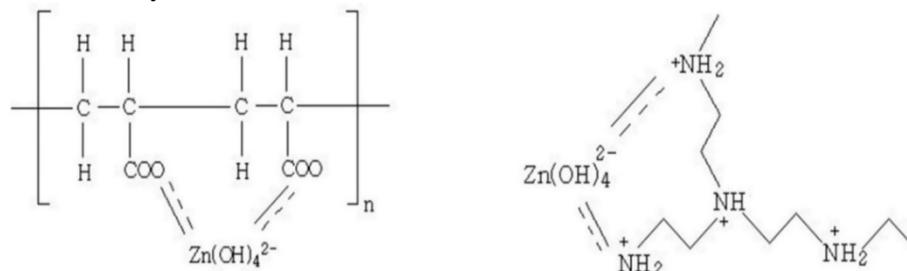


Figure 5.14. Electrostatic interactions between surface charges of ZCHH particles and of the PAAS / PEI dispersants

Mechanism of ZnO attachment to the carbon surface

According to the thermodynamic predictions performed using the HSC Chemistry software version 8 and the database (Outotec Research Center, Finland) and according to the Pourbaix diagram for the Zn-C-N-H₂O system (Figure 5.15) with Zn(NO₃)₂*4H₂O it is required a 0.01M concentration at the ionic force I = 0.03 at 250°C and a corresponding autogenous pressure of 39.23 bar, a pH greater than 8.0 for the complete precipitation of Zn ions with the formation of the Zn₅(OH)₆(CO₃)₂*2H₂O as the major phase and hydrated zinc oxide, denoted ZnO (a).

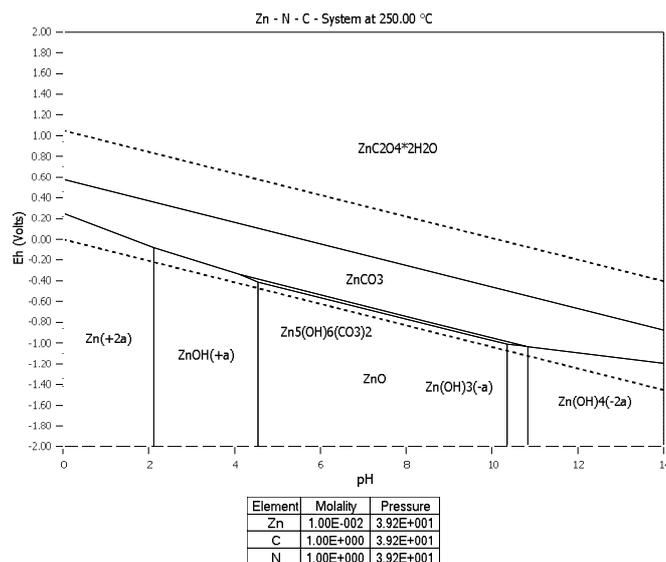


Figure 5.15. The computation of the Pourbaix diagram for the Zn-C-N-H₂O system

The equilibrium composition computed and presented in figure 5.16, shows that the hydrozincite decomposes with the formation of the ZnO solid phase, the decomposition being completed at about 400°C.

When for the hydrothermal synthesis of ZnO, urea is used as a mineralizing agent, in a first step there is obtained a hydrozincite precursor which is subsequently converted to ZnO by

The XRD pattern shows the presence of the same crystalline phases as those observed in the powder collected from the bottom of the autoclave vessel, together with the phases detected in the original carbon foam (see Table 3).

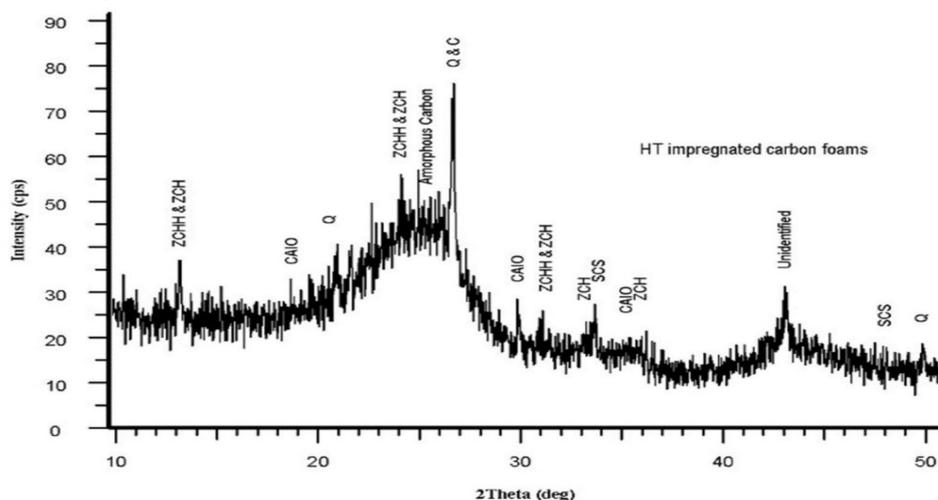


Figure 5.18. XRD phase analysis of the hydrothermally impregnated carbon foam

Table 3. XRD phase analysis of the of precipitated powder of ZnO precursors and of the impregnated carbon foam

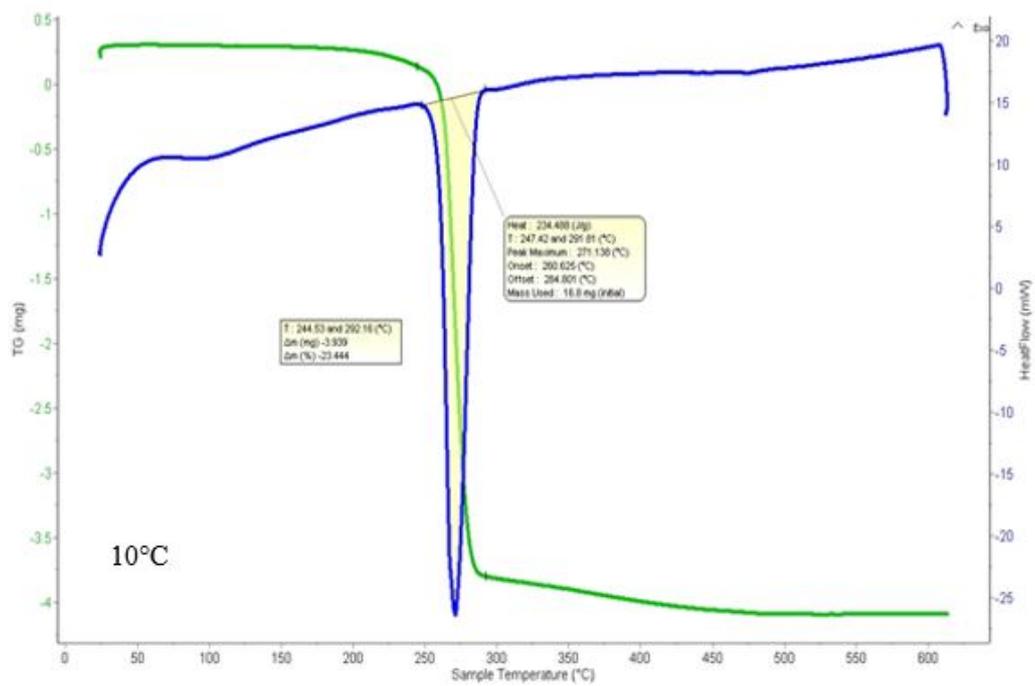
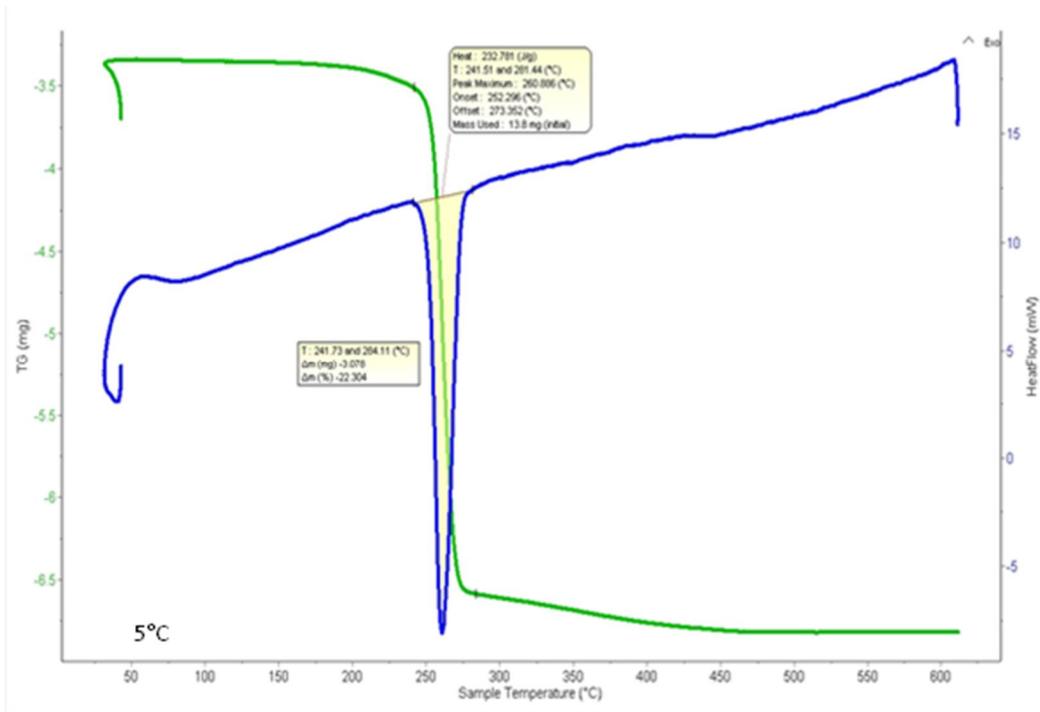
Phase / Legend XRD sample in figure 5.18	Formula	PDF reference	Content (wt. %)	
			Powder	Impregnated foam
Hydrated zinc hydroxi carbonate / ZCHH	$Zn_4CO_3(OH)_6 \cdot H_2O$	00-011-0287(Q)	t.p. major	p.
Zinc hydroxi carbonate / ZCH	$Zn_5(OH)_6(CO_3)_2$	00-054-0047(Q)	t.p.	p.
Zinc hydroxide / ZH	$Zn(OH)_2$	00-020-1435 (I)	1 - p	n.d.
Amorphous			-	t.p, major
Carbon / C	C	00-041-1487 (I)	-	p.
Quartz / Q	SiO_2	01-079-1910	-	~ 1
Sodium Calcium Silicate /SCS	$Na_{15.6}Ca_{3.84}(Si_{12}O_{36})$	01-075-1332	-	Presumptive
Calcium Aluminum Iron Oxide /CAIO	$Ca((Al_{1.817}Fe_{0.183})O_4)$	01-070-7252	-	Presumptive

Note: **p** – phase content from 1 too few per cents; **t.p.** – tens of per cents. Presumptive: phases with similar formula can exist as mixtures resulted from the synthesis of carbon foams

Figure 5.19 shows the DSC-TG spectra at a heating rate of 5°C, 10°C and 20°C per minute, recorded for the zinc oxide powder obtained by hydrothermal synthesis with urea. These spectra exhibit a sharp endothermic peak at a temperature of about 270°C (see Table 4) due to the decomposition of zinc hydroxide carbonate having an enthalpy of about 88 J/g (7.16 kJ/mol ZnO) and a total mass loss of approximately 23% (see Table 4).

Table 4. Description of endothermic peak and mass loss (DSC-TG analysis at different heating rates) for zinc oxide powder obtained after hydrothermal synthesis with urea

No.	Sample, heating rate	Temperature [°C]	Mass loss [%]
1	ZnO-U, 5°C/min	260.886	-22.304
2	ZnO-U, 10°C/min	271.138	-23.444
3	ZnO-U, 20°C/min	281.024	-23.239



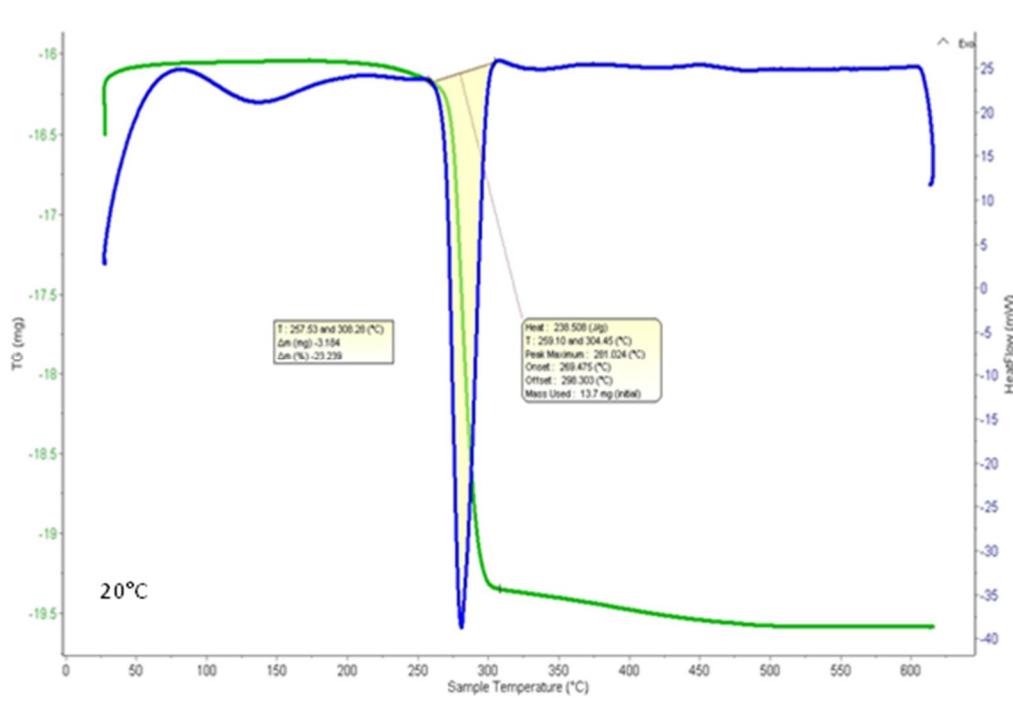


Figure 5.19. The DSC-TG curves of the zinc oxide powder obtained after hydrothermal synthesis with urea, recorded at different heating rates: 5°C, 10°C and 20°C per minute

The carbon foam samples used in the present study had a thermal conductivity of 0.31 W/m/K, a bulk density of 0.32g/cm³, a total porosity of 86%, and an average pore size of about 803 μm.

The optical micrograph of Figure 5.20 shows the presence of ZnO coating on impregnated carbon foams after heat treatment for 2 h at 500°C. The SEM micrographs in Figure 5.21 show the formation of ZnO nanopowders with “flower-like” morphology after thermal treatment of impregnated carbon foams.

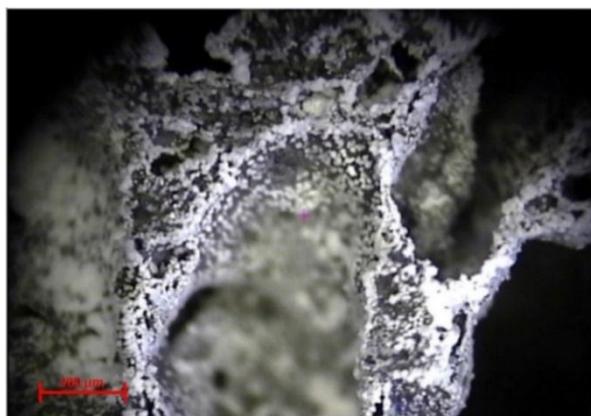


Figure 5.20. Optical micrograph of impregnated carbon foam showing the presence of ZnO white particles fixed inside the macropores

The results from XRD, thermal analysis, optical microscopy confirmed the attachment of ZnO nanoparticles to surface of the pores of the carbon foams, during the hydrothermal impregnation. The attachment took place through the following steps:

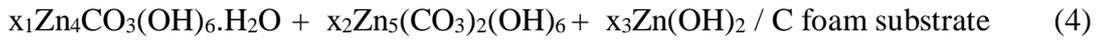
- First of all the urea decomposition in the hydrothermal solution occurs according to the following reaction:



- The formation of zinc hydroxide carbonate as the major solid phase and of a minor zinc hydroxide phase (as shown in the analysis of the XRD spectrum) takes place according to the following general reactions:

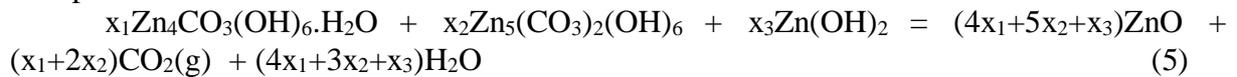


- The attachment of zinc hydroxide carbonate and of the zinc hydroxide to the carbon substrate:



where x_1 , x_2 and x_3 represent the mass% of ZCHH, ZCH and respectively ZH.

- The complex decomposition of zinc hydroxide carbonates deposited on the walls of carbon foams, by heat treatment at temperatures in the range of 250-400°C produces zinc oxide nanoparticles:



Hydrated zinc hydroxide carbonate spontaneously nucleates from the solution into multi-nuclei aggregates. These serve as sites for ZnO 1D growth in the [001] direction forming "flower-like" nanostructures of hexagonal pyramids as seen in the SEM micrographs in Figure 5.21.

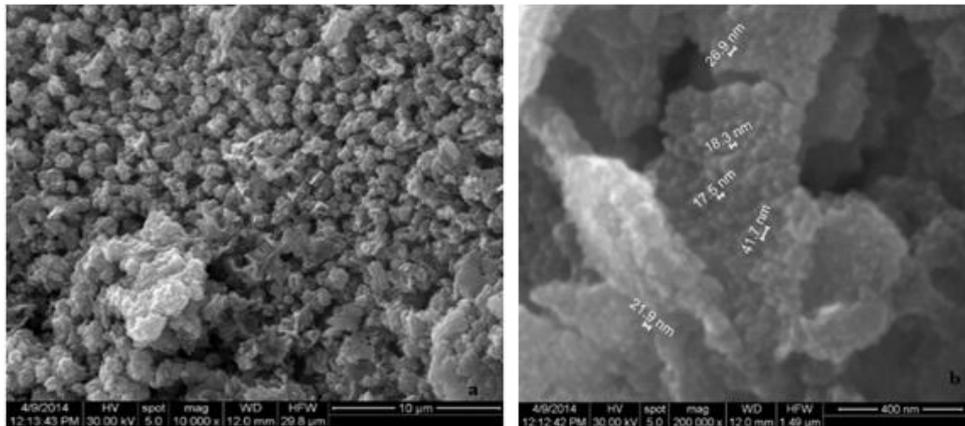


Figure 5.21. SEM on impregnated carbon foams at various magnifications: a) 10,000x shows the coated surface of the carbon foam; b) 200,000x shows the growth of "flower-like" ZnO nanocrystallites

EDAX analysis confirms the presence of ZnO on the inner surface of pores of the carbon foam (Figure 5.22).

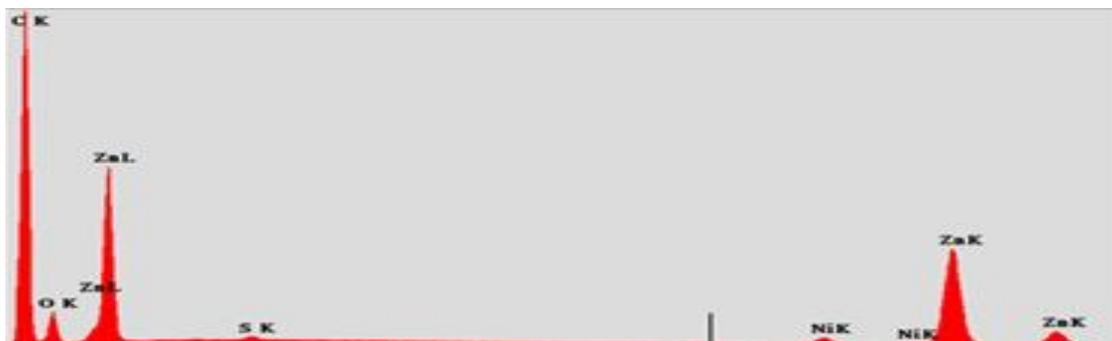


Figure 5.22. EDAX of ZnO on the inner surfaces of the carbon substrate

Chapter 6. The fictionalization of the carbon foam surface with nanoparticles

Improving the thermal conductivity of M.A.S.A.

The development of carbon surfaces with super-hydrophobic characteristics was done by coating the graphite foams and the carbon foils, respectively, with a nanostructured material (mainly nanostructured ZnO) with controlled surface texture.

There have been carried out experimental works concerning the impregnation (under hydrothermal conditions) and the coating (spraying, immersion) of graphite substrates with nanostructured materials based on pure ZnO, pure TiO₂ and a composite material made up of ZnO-TiO₂. The comparative study of the surfaces thus obtained showed pure zinc oxide (zincite structure) as the main candidate for the impregnation / coating material, as it was the only one that developed a flower-like morphology as indicated by SEM investigations. In the case of commercial graphite foils, a new coating method has been approached. The carbon substrates were immersed in aqueous ZnO suspensions and subsequently dried, this cycle being repeated. The morphology of the new surfaces was compared to that of the samples prepared by spraying.

The physico-chemical processes at the carbon / ZnO nanoparticle interface were investigated by DSC-TG measurements in the temperature range of 20-600°C. It is worth mentioning that for the synthesis of nanostructured zinc oxide, hydrothermal treatment of the inorganic precursors obtained from zinc nitrate and urea was followed by thermal treatment at 400°C.

The surface morphology of the as obtained samples was analyzed using SEM microscopy and optical microscopy. Preliminary work was undertaken to assess the hydrophobicity of these surfaces by measuring the contact angle. Samples have been functionalized with nanostructured particles of pure ZnO, pure TiO₂ and ZnO-TiO₂ composite particles.

Impregnation of graphite foams with ZnO and TiO₂

C1 foam was subjected to hydrothermal-electrochemical impregnation using the chrono-amperometry method. The use of TiO₂ in the impregnation of the carbon foam has led to similar results to those obtained when using pure ZnO. The optical micrographs of the C1 foam impregnated under hydrothermal conditions indicated the formation of discontinuous films on the pore surface.

C2 foam was impregnated with ZnO under hydrothermal conditions. The flower like structure developed by zinc oxide has been preserved. Larger pores of C2 foam seem to provide a higher degree of coverage compared to C1 foam.

The SEM analysis clearly shows the presence of the flower-like morphology in the case of the ZnO crystals impregnated in the C1 foam - Figure 6.1.

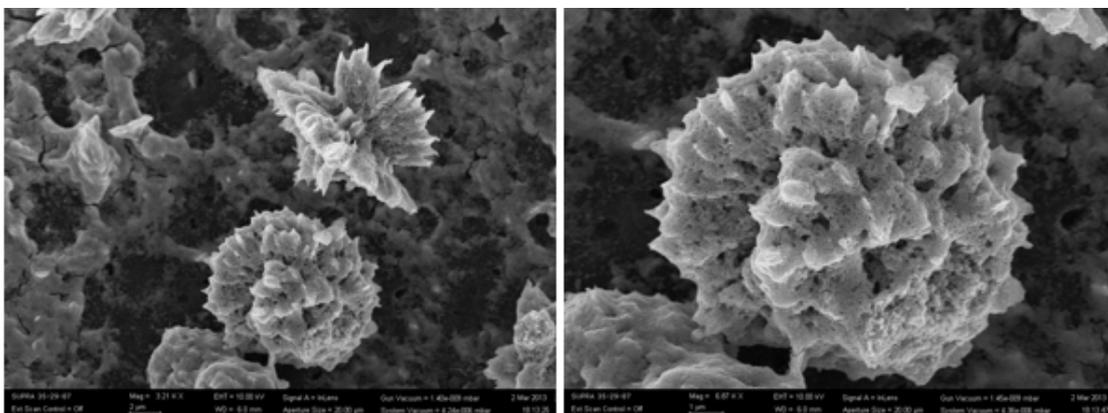


Figure 6.1. SEM analysis of ZnO crystals impregnated in C1 foam

Spraying deposition

The coatings deposited on the commercial graphite foils were obtained by spraying the stable suspensions ZnO, TiO₂ and ZnO-TiO₂. The deposition of ZnO by this method appears to be influenced by the reagents used in hydrothermal powder synthesis. The material obtained in the presence of urea was very difficult to deposit - only SEM investigations revealed the presence of flower-like crystals, randomly distributed on the graphite surface - see figure 6.2. ZnO synthesized in the presence of ammonia was easily deposited. There have been obtained discontinuous layers (having a maximum thickness of 42 μm) consisting of submicron ZnO crystals, as shown in figure 6.3.

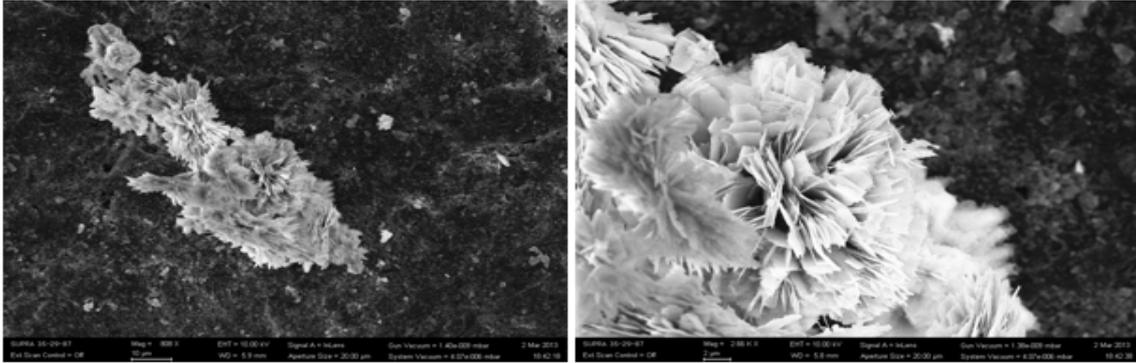


Figure 6.2. SEM micrographs – ZnO flower –like crystals randomly deposited on the graphite foil

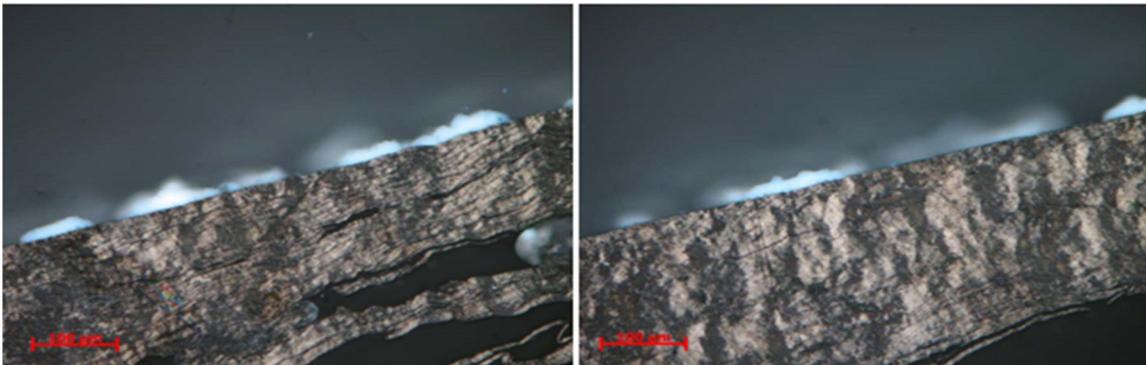


Figure 6.3. Discontinuous ZnO layer on carbon foil - N+, reflected light

Spraying of TiO₂ slurries has led to the formation of coatings with variable thickness (tens of microns) but much more compact compared to ZnO-TiO₂ deposits. Optical micrographs are shown in Figure 6.4.

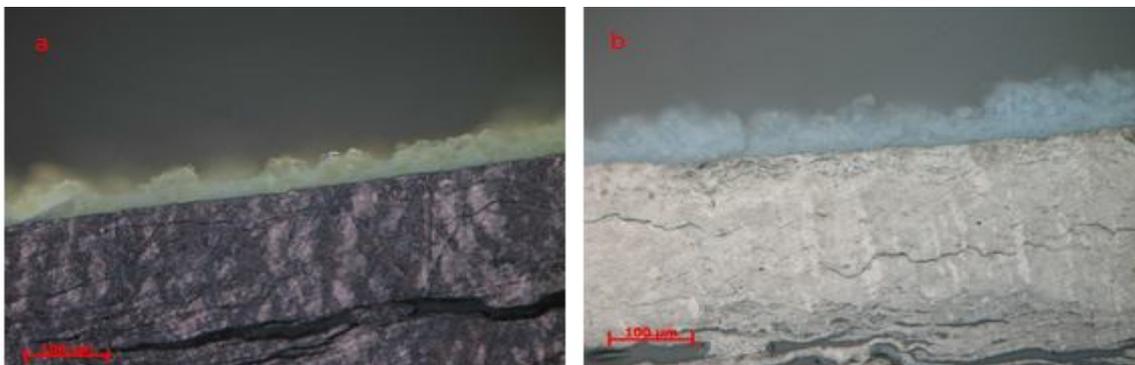


Figure 6.4. TiO₂ (a), ZnO-TiO₂ (b) coatings on commercial graphite foil- N+, reflected

The hydrothermal powder of ZnO has been used to prepare stable suspensions intended for the coating of graphite commercial films by deep-coating method. The suspension was prepared by mixing: powder, distilled water, ethyl alcohol, PAAS and NaCl solution. Successive layers were prepared by successively immersing the substrate in suspension followed by drying at 70°C. Figure 6.5 shows the SEM micrograph of the ZnO deposition on the carbon foil. SEM analysis shows the preservation of the flower-like structure but indicates the increase of ZnO both as lamellae and as needles - see Figure 6.6. Even if the film is discontinuous, immersion deposition (Figure 6.7 - left) ensures a superior coating of the graphite film compared to spray deposition (Figure 6.7 - right).

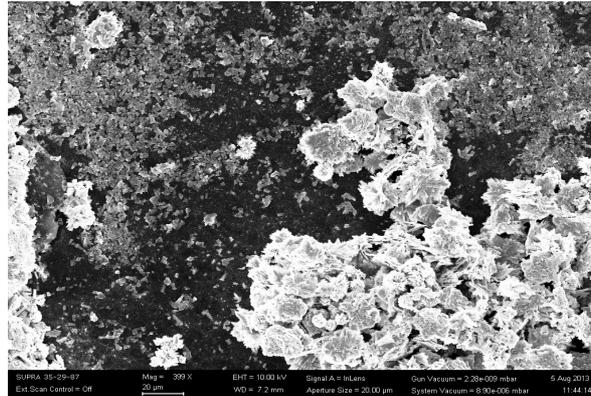


Figure 6.5. ZnO coating on graphite foil (5 cycles of immersion + drying, followed by thermal treatment at 400°C/10 min)

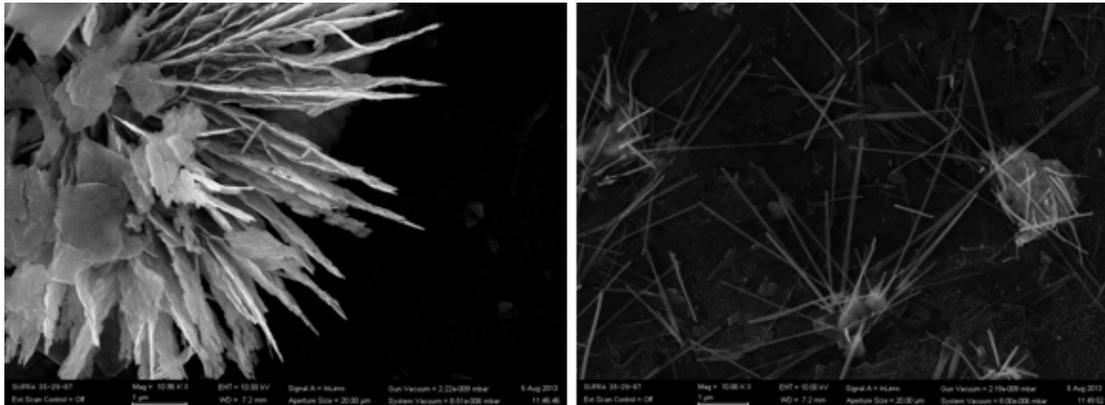


Figure 6.6. Flower-like structure developed by ZnO (grew as lamellae and needle shape)

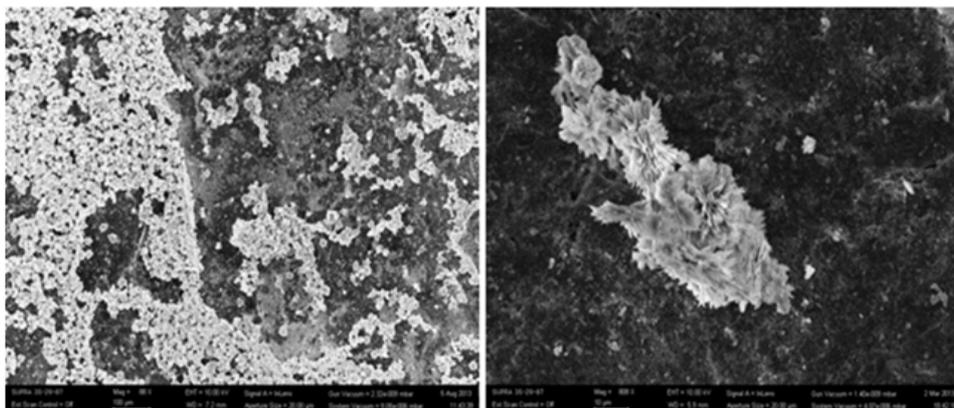


Figure 6.7. Comparative analysis of the deposition methods used during experimental works

Although it is evident that the spraying of titanium dioxide slurries provides a higher degree of overcoating compared to that of pure ZnO deposits, it has been decided to abandon the TiO₂-based compositions since this does not lead to the formation of a flower-like structure as is the case with ZnO. The SEM investigations in Figure 6.8 highlighted the presence of TiO₂ in the form of polyhedral nanometric crystals in the deposits obtained by spraying.

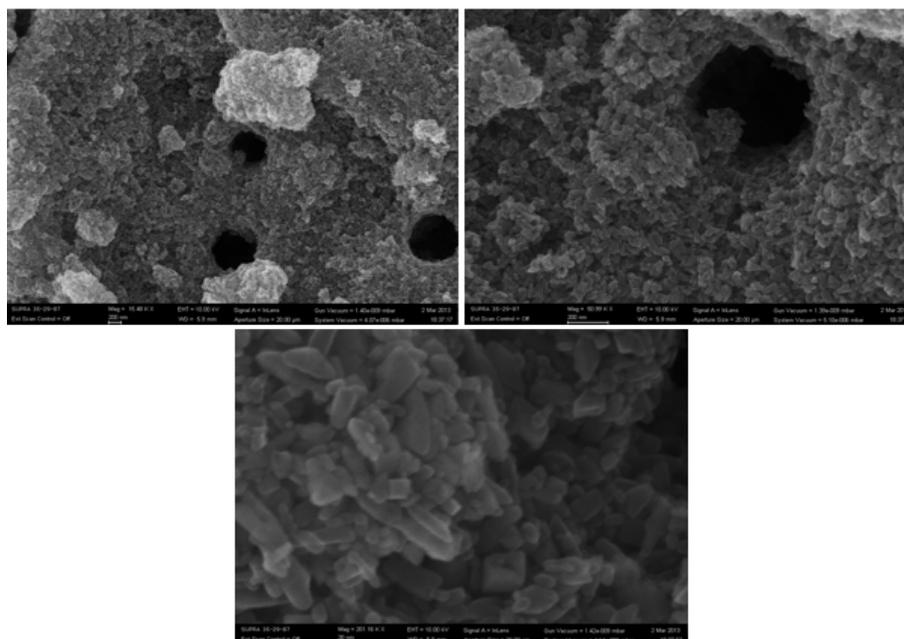


Figure 6.8. SEM images of the TiO₂, based coating, prepared by spraying

Thermal properties of coated carbon substrates - DSC-TG measurements

The DSC-TG analysis of the studied samples was performed using a SETSYS Evolution equipment, Setaram, France. The measurements were carried out in the temperature range of 25 - 600°C at various heating rates. Figures 6.9 and 6.10 graphically show the thermal effects recorded for CN3 foam (carbon foam boiled in nitric acid for 1h).

Table 5. Results of DSC measurements for CN3 sample

Sample / heating rate	Peak 1		Peak 2		Peak 3		Mass loss %
	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	
CN3 / 5°C/min	23,092	74,642	4,979	181,875	0,506	490,734	-11,855
CN3 / 10°C/min	16,525	92,313	3,945	194,039	-	-	-9,738
CN3 / 20°C/min	24,755	107,076	21,679	217,18	2,781	349,262	-11,418

CN3 sample - interpretation of the results of DSC analysis: the first endotherm peak corresponds to desorption / evaporation of water / solvent adsorbed by the material; the second effect could be the consequence of rearranging the small quantities of metallic additives used in the synthesis process; the third endothermic effect could be attributed to a possible softening of the material.

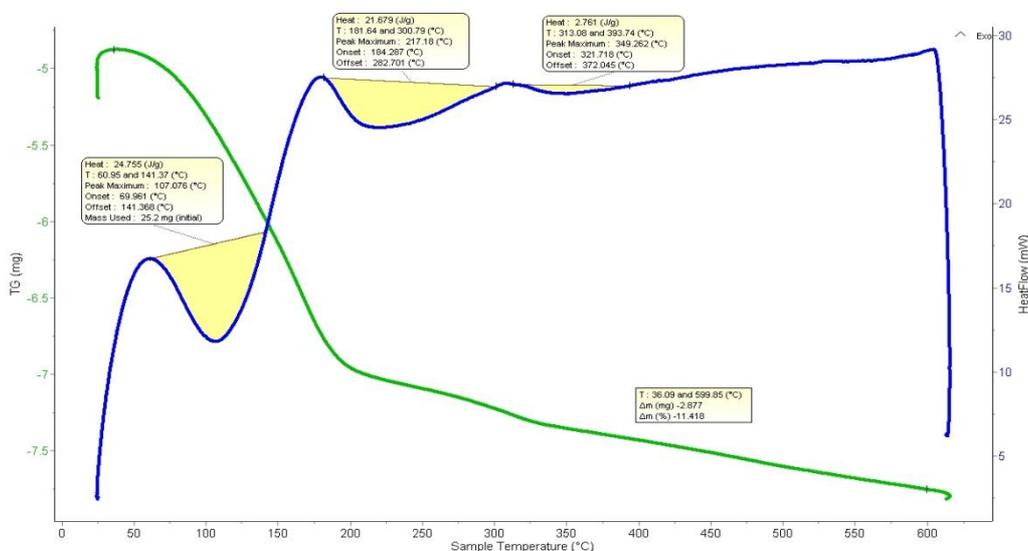


Figure 6.9. DSC-TG curves for CN3 sample

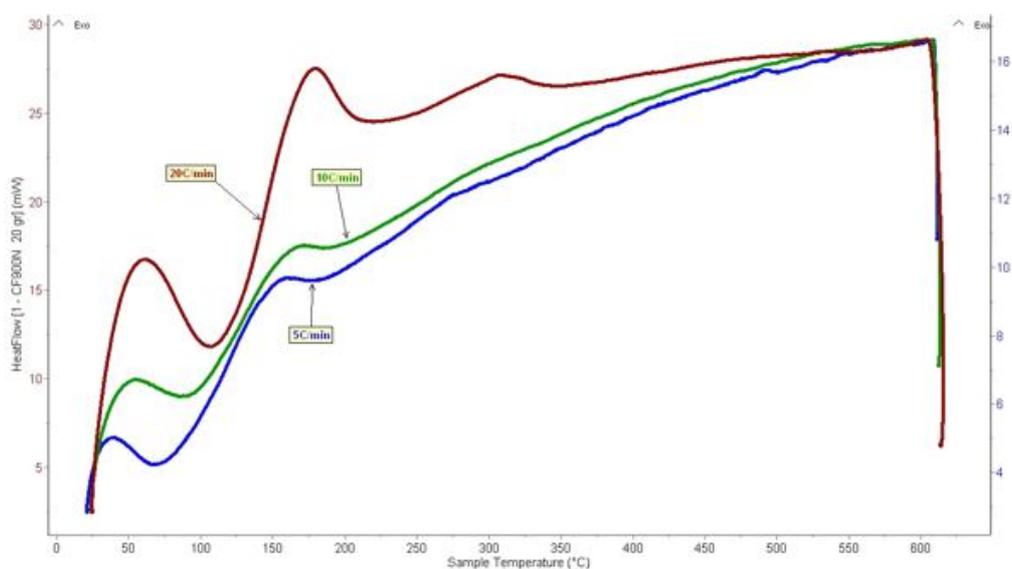
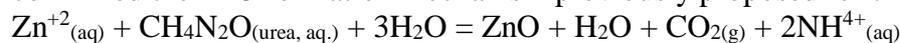


Figure 6.10. Thermal effects recorded for CN3 sample, at different heating rates

The hydrothermal nanopowder analysis (Table 6 together with Figures 6.11 and 6.12) confirmed the ZnO formation mechanism previously proposed for the hydrothermal process:



The endotherm peak observed at about 270°C corresponds to the decomposition of the $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ intermediate complex compound to ZnO.

Table 6. Results of DSC measurements for hydrothermal ZnO powder

Sample / heating rate	Peak 1		Peak 2		Peak 3		Mass loss %
	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	
ZnO-U1 / 5°C/min	232,781	260,886	-	-	-	-	-22,304
ZnO-U1 / 10°C/min	234,486	271,138	-	-	-	-	-23,444
ZnO-U1 / 20°C/min	238,508	281,024	-	-	-	-	-23,239

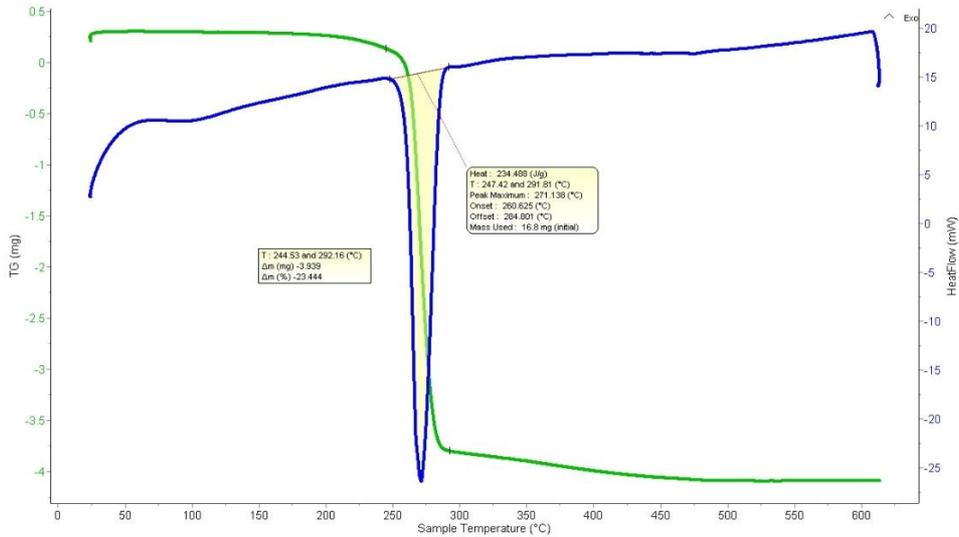


Figure 6.11. DSC-TG curves of the nanostructured ZnO powder

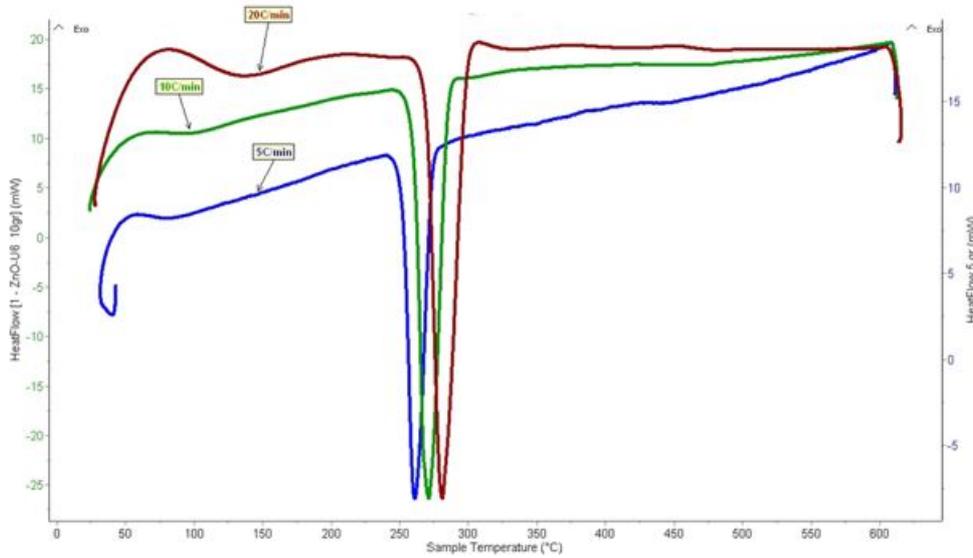


Figure 6.12. Thermal effects recorded for the nanostructured ZnO powder, at different heating rates

Figures 6.13, 6.14 and Table 7 show the results of DSC-TG measurements recorded for the CN3 foam impregnated with ZnO nanoparticles (sample code: ZnO-U1 / CN3). The first two peaks are attributed to the thermal effects corresponding to CN3 foam. The third peak indicates the ZnO formation. The third foam effect seems to be annihilated by the formation of ZnO coating.

Table 7. Results of DSC measurements for hydrothermal ZnO powder

Sample / heating rate	Peak 1		Peak 2		Peak 3		Mass loss %
	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	
ZnO-U1/CN3/5°C/min	29,348	81,613	-	-	-	-	-6,917
ZnO-U1/CN3/10°C/min	8,119	74,631	-	-	-	-	-5,91
ZnO-U1/CN3/20°C/min	28,962	90,326	1,066	142,847	0,452	298,687	-6,611

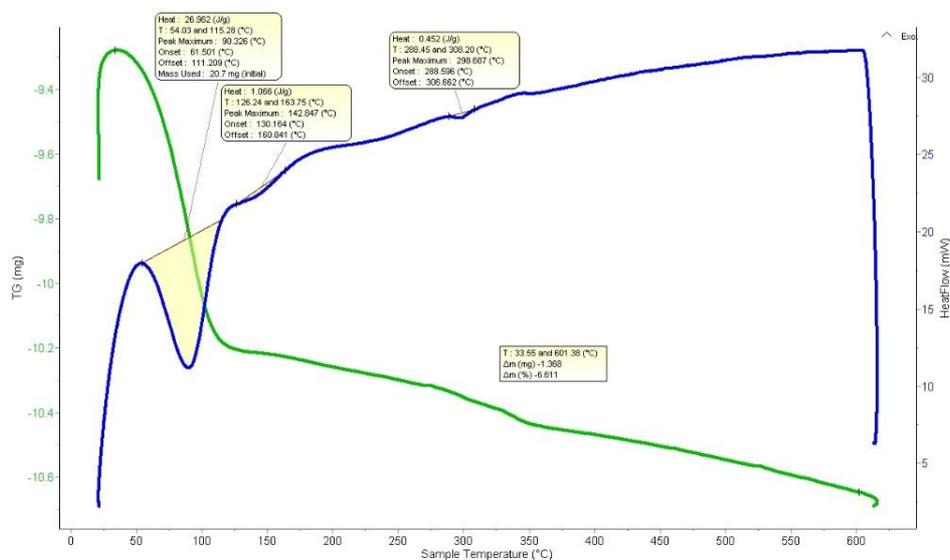


Figure 6.13. DSC-TG curves for ZnO-U1/CN3 sample

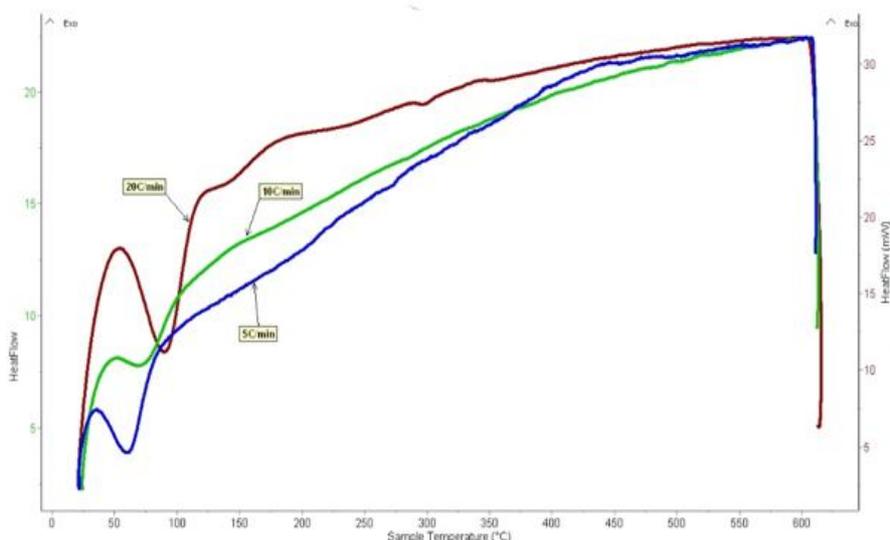


Figure 6.14. Thermal effects recorded for the sample ZnO-U1/CN3, at different heating rate

Figures 6.15, 6.16 and 6.17 and Table 8 show the results of the DSC-TG measurements recorded for the commercial carbon foil that was treated 1h in nitric acid (sample code C4) and for the same material coated with ZnO nanoparticles by immersion method. The observed endothermic peak is associated with the removal of OH groups.

Table 8. Results of DSC measurements for the graphite foil, before and after ZnO coating (immersions)

Sample / heating rate	Peak 1		Peak 2		Peak 3		Mass changes %
	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	H [J/g]	Tmax [°C]	
ZnO-U2/C4/ 20°C/min	25,282	132,642	-	-	-	-	1,057
C4 / 20°C/min	38,334	136,089	-	-	-	-	0,92

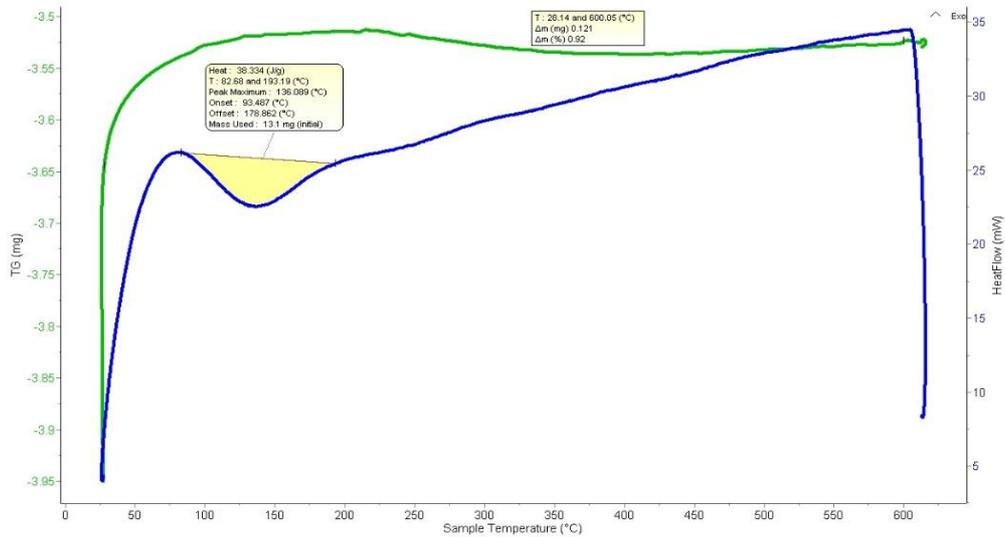


Figure 6.15. DSC-TG curves of the carbon foil - C4 sample

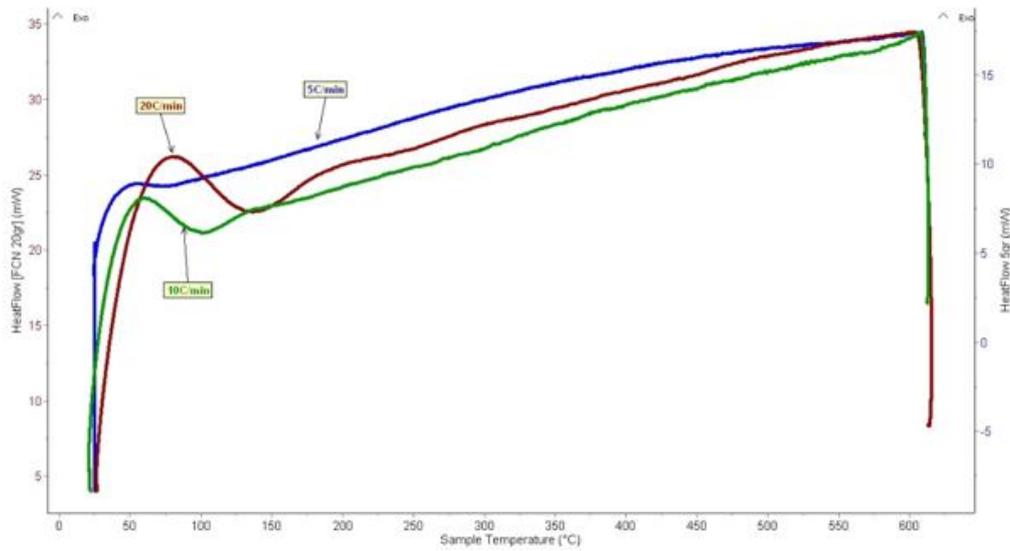


Figure 6.16. Thermal effects recorded for the carbon foil – C4 sample, at different heating rates

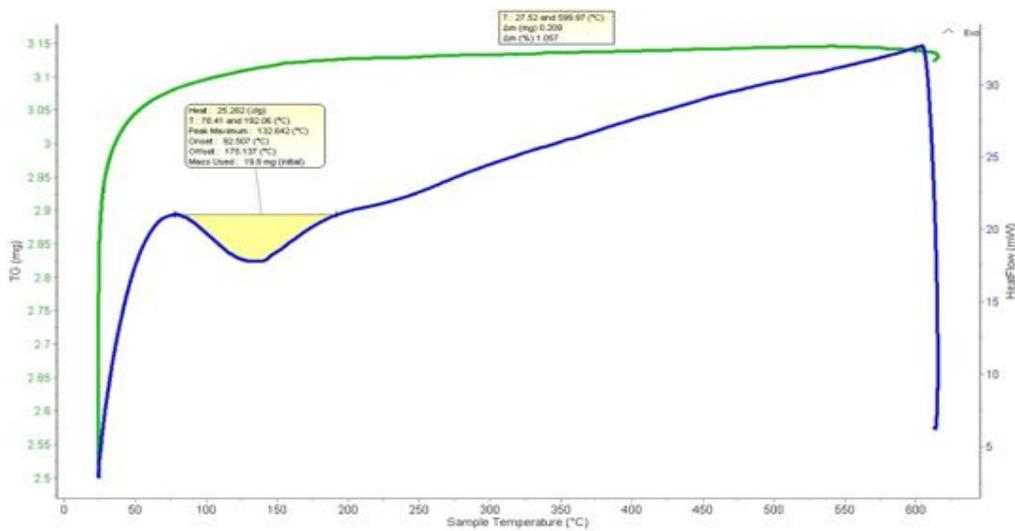


Figure 6.17. DSC-TG curves for the C4 sample coated with ZnO (dip-coating)

Hydrophobic character of coated carbon substrates – the contact angle measurement

The experiments were carried out on samples of commercial carbon foil (sample code FC) and ZnO coated (immersion) on carbon foil which was thermally treated (ZnO / FC-TT, sample code P4). Contact angles of water, glycerol and aqueous solutions of Mannitol (10% and 15%) were measured. The water and glycerol experiments are presented in Figures 6.18, 6.19, 6.20, 6.21 and the results of these measurements are given in Table 9.

It is observed that depositing a zinc oxide layer on the surface of the carbon foil changes the contact angle values for both water and glycerol to higher values. If glycerol wets both samples, in the case of water the ZnO layer induces a slightly hydrophobic behavior for the studied sample.

Table 9. Results concerning the hydrophobic character of the FC and P4 samples

Sample	Contact angle [°] water	Contact angle [°] glycerol	Surface tension γ [mN/m]	Dispersive part of γ γ^d [mN/m]	Polar part of γ γ^d [mN/m]
FC	88,7	59,4	75,3	75,1	0,2
P4	94,2	75,5	38,8	38,3	

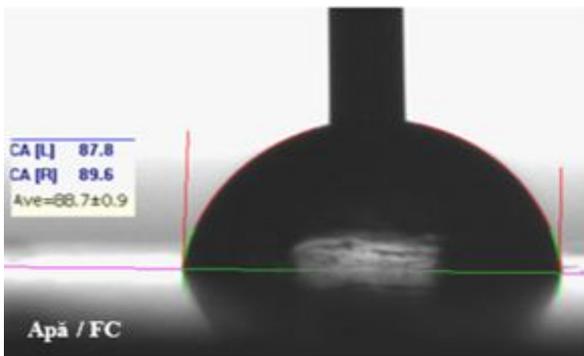


Figure 6.18. Contact angle evaluation - water/FC

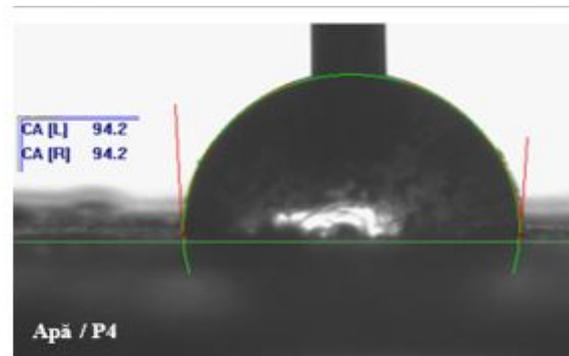


Figure 6.19. Contact angle evaluation - water//P4

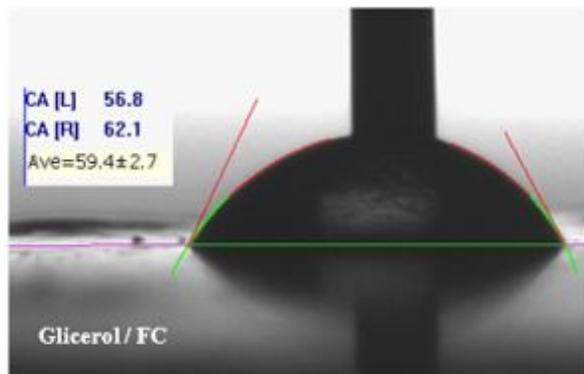


Figure 6.20. Contact angle evaluation - glycerol/FC

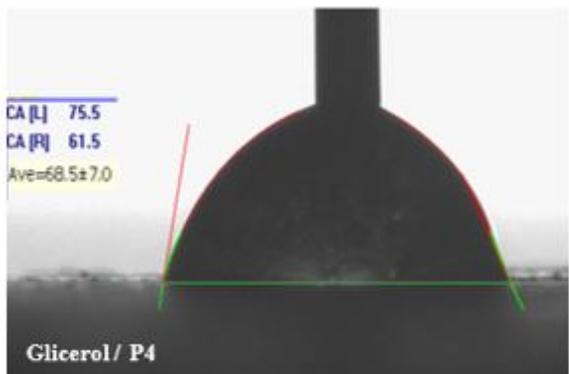


Figure 6.21. Contact angle evaluation - glycerol/P4

This behavior of the P4 sample was also observed in experiments with aqueous mannitol solutions (Figure 6.22). As it can be seen from table 10, the values of contact angle formed between the sample and water, sample and 10% mannitol solution and 15% mannitol solution respectively are greater than 90°.

Table 10. The slightly hydrophobic behavior developed by the ZnO coating in the presence of aqueous solutions

Studied system	Contact angle [°]		
	Left	Right	Average
Water / P4	94,2	94,2	94,2
10% Mannitol / P4	95,7	95,7	95,7
15% Mannitol / P4	98,5	92,4	95,5

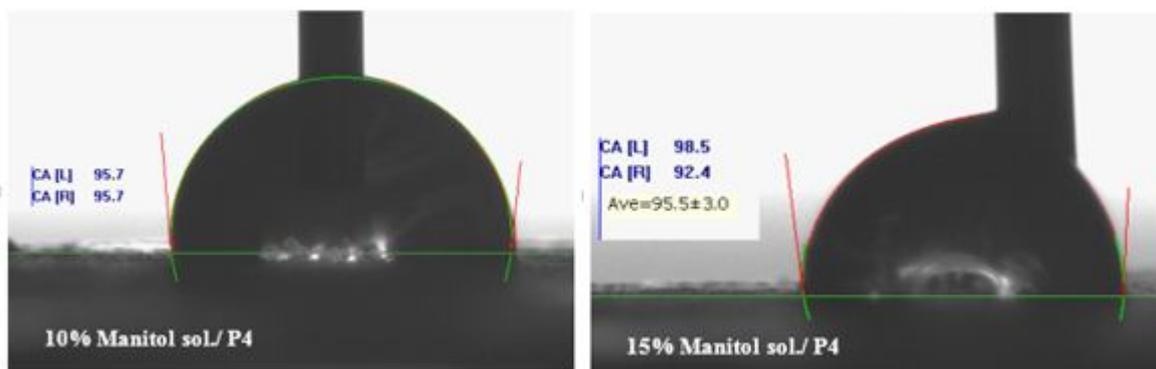


Figure 6.22. The evaluation of the contact angle formed by various aqueous solutions with the graphite foil coated with a nanostructured ZnO layer

Impregnation and attachment of ZnO nanoparticles to graphite foams

The impregnation and functionalization experiments were carried out on the latest generation of carbon foam, C3-S samples received from CNRS / IJL.

In particular, the high open porosity of approximately 86% was exploited during the proposed hydrothermal impregnation process by increasing the concentration of Zn in the solution in order to increase the thickness of the deposited ZnO coating, as it can be seen in Figure 6.23.a.

Table 11 shows the samples coated with different concentrations of Zn (II). A series of optical micrographs of C foam before and after impregnation with various concentrations of ZnO are shown in figures 6.23.b, 6.23.c and 6.23.d.

Table 11. ZnO hydrothermal impregnation of the C foam

Impregnated foam substrate	Zn(II) concentration [Mol/l]	Figure
C3-S		6.29a
C3-S	0.1	6.29b
C3-S	0.2	6.29c
C3-S	0.3	6.29d

It can be seen that increasing the concentration of Zn in the impregnation solution increases the degree of surface coverage. For the sample hydrothermally treated with 0.1M zinc nitrate solution, the ZnO coating is discontinuous. When the Zn concentration increases to 0.2 and 0.3M, the ZnO coating appears both on the sides and at the base of the pores, in some cases closing the open pores. However, it is not possible to estimate the mass increase due to the loss of fine particles of C during the nitric acid treatment before deposition and also during the hydrothermal treatment. XRD analysis indicates the initial formation of both hydrated zinc hydroxycarbonate and zinc hydroxide which are converted to ZnO (zincite) after heat treatment.

The surface potential and the hydrodynamic diameter of the hydrated zinc hydroxycarbonate particles obtained by hydrothermal treatment represent a crucial factor in the binding of ZnO nanoparticles to the surface of carbon foam, due to the high influence on particle mobility and the electrostatic interactions with the substrate.

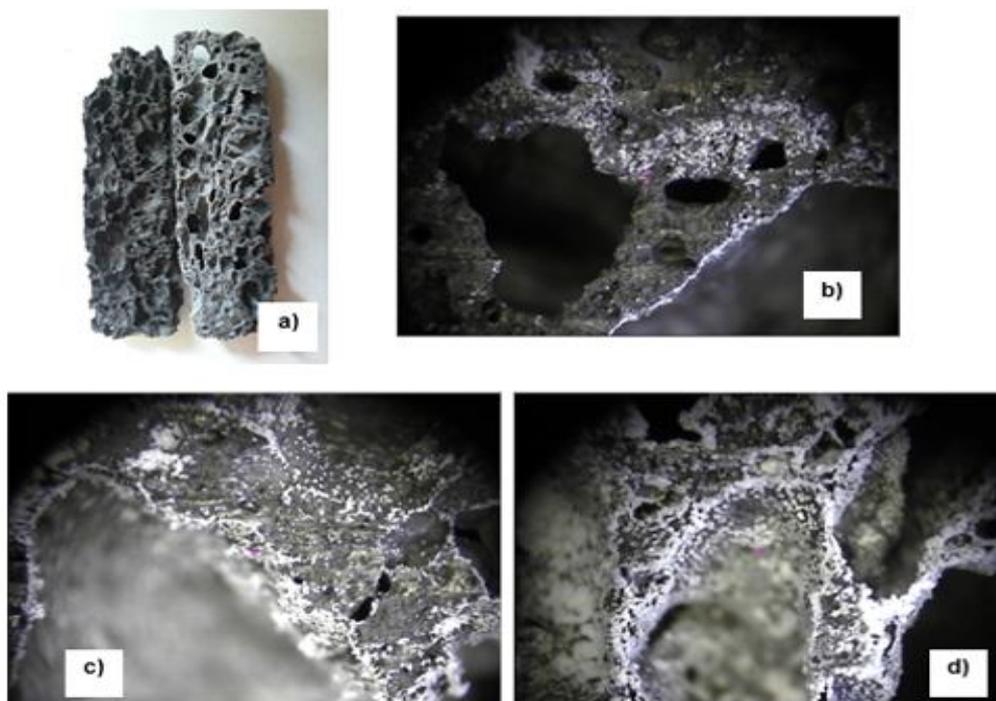


Figure 6.23. Optical microscopy performed on C3-S carbon foams impregnated with different Zn concentrations: a) optical appearance of foam uncoated and coated with 0.3M Zn; b) carbon foam coated with 0.1M Zn; c) foam coated with 0.2M Zn; d) C foam coated with 0.3M Zn

The evaluation of the zeta potential of colloidal suspensions was performed with the Malvern Zetaseizer ZS90 equipment (with auto-titration), using HNO₃ and NaOH for pH control. The results are shown in Figure 6.24. A negative value of the zeta potential for the entire pH range is observed. The steady decrease in the potential is highlighted by the increase in pH. Alkaline pH due to urea decomposition provides negative values of the surface potential and avoids the agglomeration of the dispersed zinc carbonate particles.

The formation of ZnO deposition on the carbon surface is also observed with the help of the FT-IR spectrum in Figure 6.25. It can be noticed that the bands of carbonyl bond observed for the nitric acid-treated carbon foams (Figure 6.25a) are diminished after ZnO nanoparticles are bound and the band for the Zn-O bond at 964 cm⁻¹ appears (Figure 6.25b).

The shape and morphology of ZnO deposited on the carbon surface after heat treatment were investigated by SEM analysis (at different magnifications). The micrographs are presented in Figure 6.26.

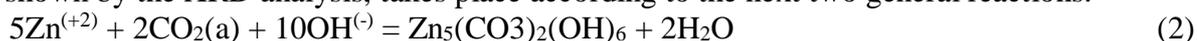
Figure 6.26a shows that the use of a 0.3M Zn solution leads to the full coverage of the carbon foam surface with ZnO. At higher magnification the flower morphology can be observed and details of the investigated samples are highlighted. Figure 6.26d shows that this flower structure is made up of individual crystals with dimensions in the range 17-27 nm.

Starting from the thermodynamic modelling which was performed using the specialized HSC v.7.0 software, it was proposed a mechanism to explain the ZnO nanoparticles attachment on the inside surface of carbon foam:

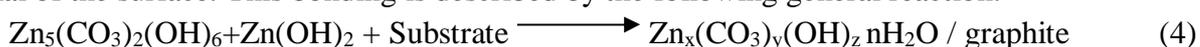
The first step is the hydrothermal decomposition of urea according to the following reaction:

$$\text{CO}(\text{NH}_2)_2 + 3\text{H}_2\text{O} = \text{CO}_2(\text{g}) + 2\text{OH}^{(-)} + 2\text{NH}_4^{(+)} \quad (1)$$

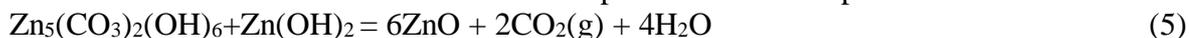
The formation of hydro-zincite as major phase and of the zinc hydroxide as secondary phase, as it is shown by the XRD analysis, takes place according to the next two general reactions:



The hydrated zinc carbonate complex bonds to the graphite substrate due to the negative potential of the surface. This bonding is described by the following general reaction:



Finally the carbonate deposited on the walls of the graphite foam decomposes to zinc oxide during the thermal treatment at 150-200°C. There are produce ZnO nanoparticles.



ZnO spontaneously nucleates from solution and these nuclei tend to aggregate. They serve as growing centers for 1D ZnO on the direction [001] thus forming flower-like nanostructures consisting of hexagonal pyramids as it can be seen in the SEM micrographs.

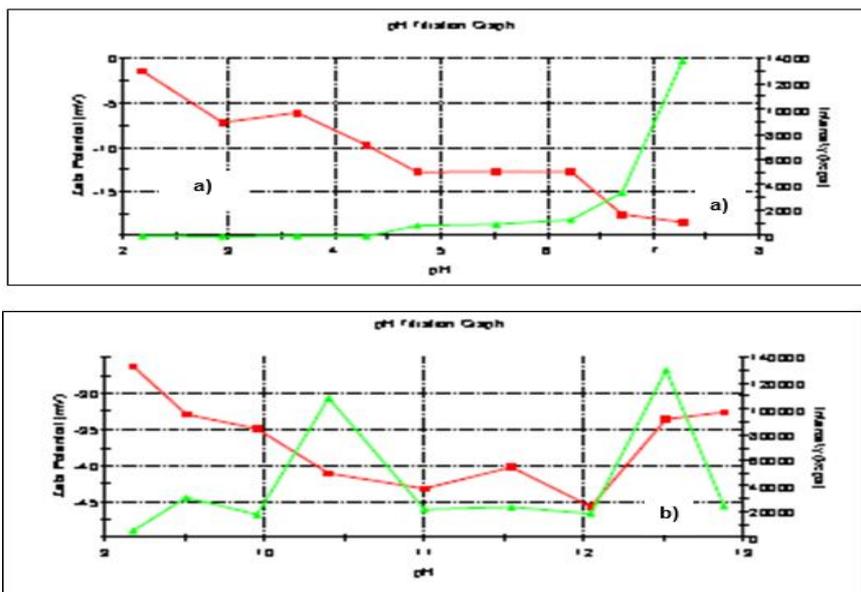


Figure 6.24. The evolution of zeta potential of the hydrated zinc carbonate precursor in acid pH during HNO_3 titration (a) and in alkaline pH during NaOH titration (b)

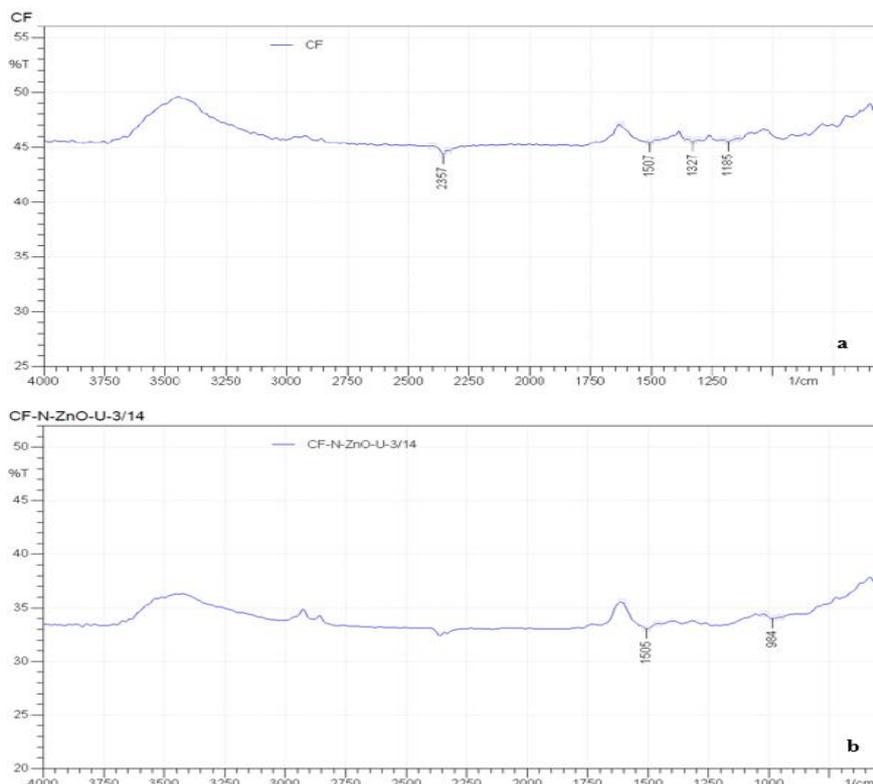


Figure 6.25. FT-IR spectrum recorded for the carbon foam (a) and for the same material impregnated with ZnO nanoparticles and subjected to heat treatment at 400°C (b)

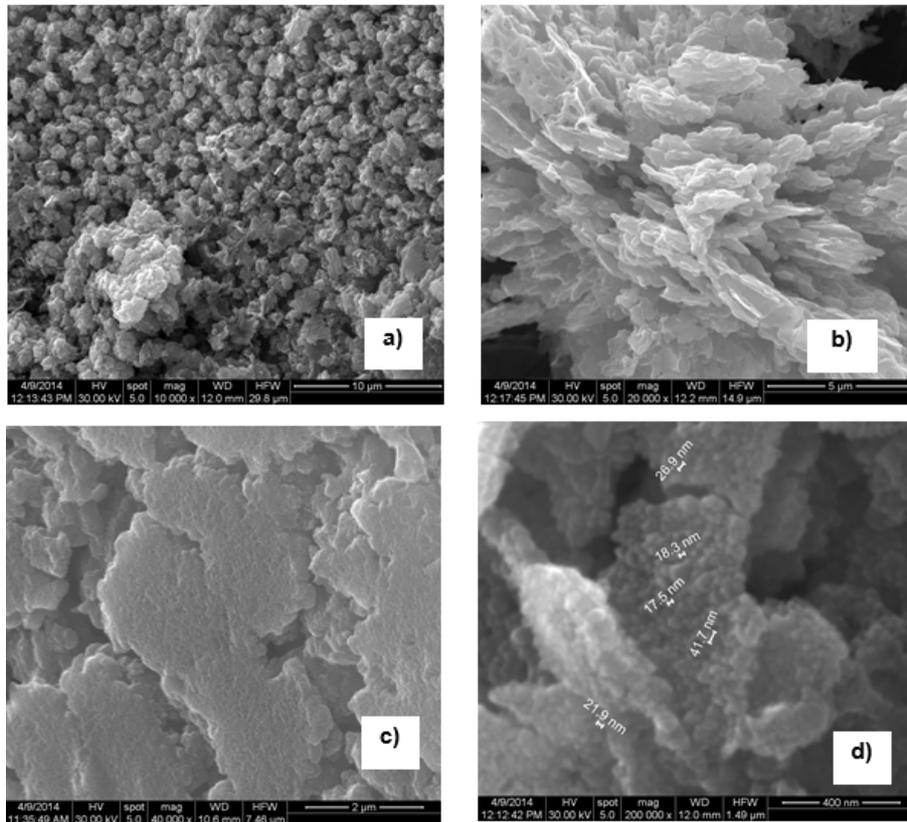


Figure 6.26. SEM micrographs of the carbon foam impregnated with ZnO – different magnifications: a) x 10,000; b) x 20,000; c) x 40,000; d) x 200,000

To study in detail the interactions occurring at the ZnO / C interface, a zinc-coated carbon particle was carefully detached from the graphite substrate. The operation was performed under the microscope. The distribution maps of C, Zn, Ni (carbon foam) and O, respectively, were recorded along this interface. Figure 6.27 shows the SEM image of a ZnO coated carbon particle extracted from the substrate and its analysis EDAX.

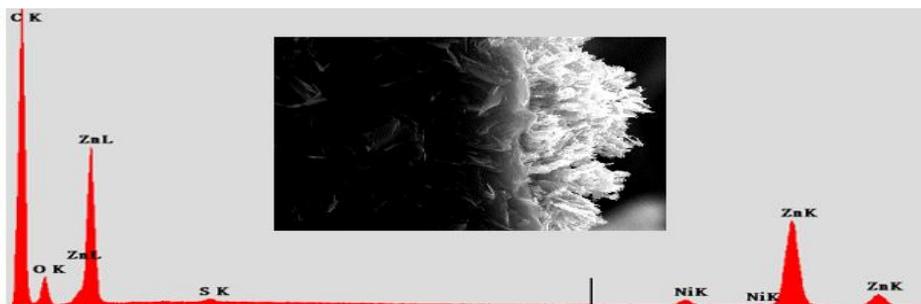


Figure 6.27. EDAX analysis of the ZnO coated carbon particle detached from the substrate

The distribution maps in Figure 6.28 show that there is no inter-diffusion between the carbon foam and the deposited ZnO nanoparticles. Figure 6.29 shows a possible mechanism that is proposed for ZnO attachment based on physico-chemical interactions on the surface. These interactions occur between the functional groups on the surface of the carbon foam and the polar plane (001) of the ZnO flower structure.

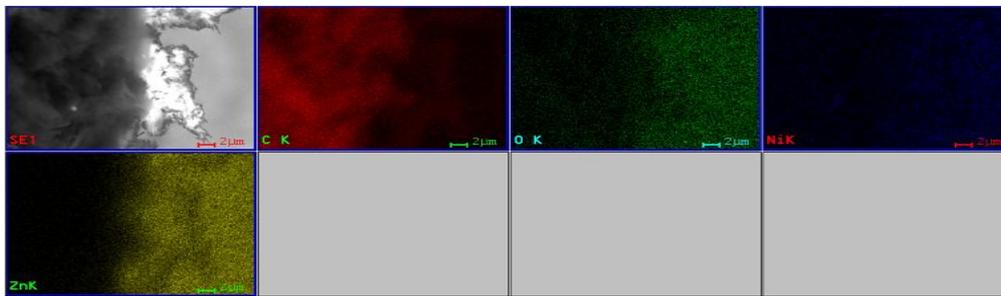


Figure 6.28. The distribution maps of C, O, Ni and Zn - ZnO coated carbon particle detached from the substrate

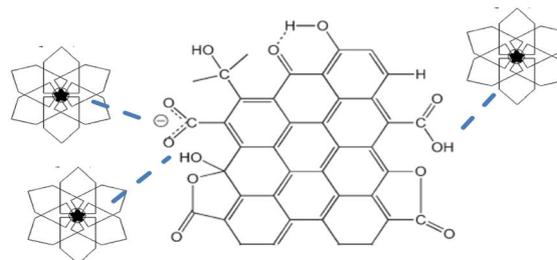


Figure 6.29. Schematic representation of the mechanism proposed for the interactions at the ZnO/carbon foam interface

Contact angle measurement – sugar alcohol / graphite foil

One of the main aspects of the thesis is to measure the contact angle of the sugar alcohol on a carbon surface covered with nanoparticles of ZnO. Since there is no data on this subject in the literature, and the measurement of this angle is very difficult on carbon foam with irregular macroporous structure, the experiments were performed on commercial graphite foils coated with ZnO nanoparticles, this oxide material being obtained using the same hydrothermal method used in the case of impregnation of the carbon foam.

Sugar alcohols studied were melted. Small droplets (2mm diameter) were dripped onto each type of substrate and the contact angle was measured using a Rame Instrument goniometer at the Institute of Materials Physics, Bucharest. Figure 6.30 shows the droplets used for determinations. Table 12 presents the results of these determinations.

The ZnO coatings deposited on the graphite foil result in a hydrophobic surface relative to xylitol and the xylitol + erythritol mixture. The non-polar sugar alcohols are expected to have a hydrophobic behavior opposite to that of water.



Figure 6.30. Contact angle of xylitol and the xylitol + erythritol mixture on carbon foils coated with ZnO dispersed in various additives

Table 12. Contact angle of sugar alcohols (from Rhodia) on C foil covered by spraying with ZnO and other additives

Substrate	Alcohol	Contact angle [°]	Remarks
Uncoated graphite foil	Xylitol	85	
Graphite foil coated with ZnO + 5%PVA	Xylitol	116	Hydrophobic
Graphite coated with ZnO + ELSW	Xylitol	112	Hydrophobic
Graphite coated with ZnO + TLS	Xylitol	81	
Uncoated graphite foil	64% Xylitol+36% Erythritol	88	
Graphite foil coated with ZnO + 5%PVA	64% Xylitol+36% Erythritol	102	Hydrophobic
Graphite coated with ZnO + ELSW	64% Xylitol+36% Erythritol	103	Hydrophobic
Graphite coated with ZnO + TLS	64% Xylitol+36% Erythritol	75	

Chapter 7. General conclusions. Original contributions. Research directions

General conclusions

- Thermal energy storage systems are classified into three groups: storage of sensitive heat, latent heat storage and thermo-chemical storage.
- Phase Change Materials (PCM) are products with a high potential for thermal management solutions, and this is due to the fact that these materials store and release thermal energy during the melting and crystallization process.
- Sugar alcohols are a class of materials that have an important application potential for the energy storage systems at medium temperatures.
- A number of experimental solutions have been studied to increase the thermal energy storage capacity using sugar alcohols-based PCMs by addressing controlled growth methods of the exchange surface while controlling the under-crystallization process.
- A simple hydrothermal impregnation process was developed to assure the functionalization of the carbon foams with nanostructured ZnO with flower-like morphology to control the properties of these surfaces, meaning to avoid the crystallization of sugar alcohols (selected as phase change materials) during thermal cycles in the thermal energy storage system.
- It was studied the functionalization of carbon materials by incorporating ZnO particles to control superficial properties at the substrate / PCM interface.
- The thermal stability of the obtained composite system has been studied by DSC thermal analysis methods.
- The in-situ hydrothermal technology proposed for the impregnation of porous graphite by the attachment of ZnO nanoparticles has been verified and the parameters of the process have been established using the new high carbon macroporous carbon foams made by CNRS / IJL Nancy, France. This allowed to increase the concentration of Zn in the impregnation solution and consequently the increase in the thickness of ZnO deposition inside the pores became evident.
- The microstructure of the obtained coatings has been studied. The coating consists of a complex mixture of two different types of zinc hydroxycarbonate (hydrated and non-hydrated) and metastable β zinc hydroxide. Following the heat treatment, the coating material completely crystallizes as zincite (ZnO), this being the only phase observed in the XRD analysis. The observation were supported by the DSC analysis.
- Results from XRD, thermal analysis and optical microscopy confirmed the attachment of ZnO nanoparticles (by hydrothermal impregnation) to inner surfaces of the carbon foam pores. EDAX analysis confirms the presence of ZnO on the inside surfaces.
- The deposition obtained by spraying the suspensions based on hydrothermal powders of ZnO onto the carbon samples is constituted as compact layers with thickness between 10 and 20 μm . These films consist of isometric crystals.

➤ The high degree of compaction of the deposits is due to the narrow size distribution of ZnO nanostructured hydrothermal powders. The good stability of the suspensions allowed them to be sprayed with compressed air.

➤ Effective open porosity (about 60%) and average pore size (> 600 microns) allow hydrothermal in-situ deposition of thin films of ZnO made up of needle-shaped crystals. Thermal treatment at $T > 300\text{ }^{\circ}\text{C}$ is required for the total conversion of zinc hydroxycarbonate into zinc oxide.

➤ The average size of hydrated zinc hydroxide carbonate particles are significantly lower than the average dimensions of the cells inside the carbon foam and their attachment inside the porosity is quite feasible.

➤ Pressure treatment at 100 atm leads to an enlargement of large pores and to a low pore shrinkage, probably due to the slight plastic behavior of the structure. The maximum pore size of L1 material increases by about 15% and the pores of C1 foam by 12.71%.

➤ The selected carbon foams were surface treated by boiling them in 1M nitric acid solution for one hour to create an additional surface of functional groups, and therefore to improve the surface capacity to assure a reactive fixation of ZnO nanoparticles. After the treatment in nitric acid, the carbon foam samples were submerged in a vertical autoclave filled with a stoichiometric solution mixture of zinc nitrate and urea. The physicochemical processes at the C substrate/ZnO nanoparticle interface were investigated by DSC-TG measurements in the temperature range 20-600°C. For the final obtaining of nanostructured zinc oxide, hydrothermal treatment of inorganic precursors obtained from zinc nitrate and urea followed by heat treatment at 400°C was performed.

➤ C1 foam was subjected to hydrothermal-electrochemical impregnation using the chrono-amperometry method. The use of TiO₂ materials in carbon foam impregnation has led to similar results to the use of pure ZnO. The optical micrographs of the C1 foam impregnated under hydrothermal conditions indicated the formation of discontinuous films on the pore surface.

➤ C2 foam was impregnated with ZnO under hydrothermal conditions (without any electrochemical process). The flower-like structure of zinc oxide has been preserved, as can be seen from the SEM micrographs. The zinc oxide lamellae have nanometric thickness. The larger pores of C2 foam seem to provide a higher degree of coverage compared to C1 foam.

➤ Although the spraying of titanium dioxide slurries provides a higher degree of coverage than pure ZnO deposits, it has been decided to abandon TiO₂-based compositions because this does not lead to the formation of a flower-like structure as is the case of ZnO.

➤ The hydrothermal powder of ZnO has been used to prepare stable suspensions for immersion coating of commercial graphite foils. The suspension was prepared by mixing: powder, distilled water, ethyl alcohol, PAAS and NaCl solution. Successive layers were deposited by immersing the substrate in suspension than drying it at 70°C. Even if the film is discontinuous, immersion deposition provides a superior coating of the graphite substrate compared to the spray deposition.

➤ There have been prepared samples functionalized with pure ZnO, pure TiO₂ and ZnO-TiO₂ composite particles.

➤ The evaluation of the contact angle showed that ZnO deposits on graphite foil lead to hydrophobic surfaces in respect with xylitol and xylitol + erythritol mixture when using the appropriate additives: PVA and water-soluble eco-lacquer. It has been concluded that in relation to non-polar sugar alcohols, coatings produce inverse hydrophobic behavior compared to water.

➤ Attaching ZnO nanoparticles with controlled morphology can improve the hydrophobic properties of graphite-based materials, as this property is determined by material surface chemistry and by the geometric structure of the surface. ZnO nanocrystals with hexagonal wurtzite structure grow along the c axis, and thus the (001) surfaces are highly polarized due to the presence of Zn²⁺ and O²⁻, while the (011) surfaces are not polarized. The very porous structure of the network of ZnO nanoflowers mainly exposes the non-polar face of the crystallites, which significantly improves the hydrophobic behavior. The final properties depend on the chemistry of the process, the nature of the dopants, the grafting agents, the solvents and the substrate.

Original contributions

✓ There were improved and developed new phase change materials intended for applications in the seasonal storage of thermal energy in the range of average temperature.

✓ There have been established the conditions for functionalization of the inner surface of the C macropores by attaching the ZnO nanoparticles: the inner surface of the carbon has functional groups that allow the interaction with the polar ZnO groups, the solution containing Zn^{2+} ions completely fills the pores of the C structure, the ZnO nucleation occurs in a proportion as high as possible in the inside pores avoiding the blocking of pore interconnection, and the solution containing Zn^{2+} ions is chemically compatible with the carbon surface (there are no chemical reactions leading to the production of byproducts and to the destruction of carbon structure).

✓ Most researches on the hydrothermal synthesis process are based on the intelligent modelling of hydrothermal reactions carried out prior to the beginning of the actual experiments. Modelling is useful for predicting experimental conditions needed to obtain the desired phase with controlled size and shape and is based on thermodynamic principles. Thermodynamic calculations are available due to the specialized software endowed with thermochemical data base, this software allowing the simulation of real conditions for the chemical reaction. The Outokumpu HSC Chemistry for Windows makes possible the calculation, the thermodynamic equilibrium study and the study of the system stability, with the help of the Pourbaix diagrams for the Zn-O-H-C-N system.

✓ Based on the thermodynamic prediction studies, a method based on the hydrothermal electrochemical deposition of ZnO which nucleates inside the macropores due to the reaction between Zn^{2+} and urea cations, was proposed. Subsequent studies and experiments have shown that nanoparticle attachment can be performed at the same synthesis parameters and in the absence of the external electric field (which could potentially improve ZnO growth).

✓ A mechanism has been proposed to explain how ZnO nanoparticles adhere to the carbon surface. The mechanism is based on the results provided by the XRD, FT-IR, SEM, EDAX, potential zeta assays and involves the following may stages: the zinc hydrocarbonate nucleation governed by the homogeneous precipitation reaction of Zn^{2+} with the urea, its attachment to the functional groups on the surface of the carbon structure and the thermal decomposition of this compound to ZnO with a flower-like structure, at temperatures higher than 200°C.

✓ Commercial graphite foils have also been coated with ZnO. The deposition was carried out by spraying dispersions containing commercial additives to control adhesion and to reduce the problems observed due to the exfoliation of the outer layer from the surface of the graphite material during the tests. Adhesion studies performed by scratch tests, have confirmed the improvement of ZnO adhesion to the substrate.

✓ The stable ZnO suspension was successfully obtained directly from the hydrothermal process and was used to obtain compact coatings by spraying with compressed air.

✓ The morphology of the surfaces of the as-prepared samples was analyzed using SEM microscopy and optical microscopy. Preliminary work was undertaken to assess the hydrophobicity of these surfaces by measuring the contact angle.

✓ For the development of carbon surfaces with super-hydrophobic properties, the carbon structures (foams and foils) have been coated with nanostructured ZnO having a controlled surface texture, by using a unique wet chemical method at high pressures. Due to the high degree of novelty, there is a lack of standardized methods to investigate the hydrophobic behavior and thermal transfer properties of the proposed C/ZnO/sugar alcohols systems.

Research Directions

1. The methodology proposed for the contact angle measurement for the sugar alcohol will continue in order to check the results reproducibility by errors analysis. The temperature influence will be approached.

2. The adhesion energy of the ZnO nanoparticles to the surface macroporous carbon will be evaluated by precise calorimetric measurements. Comparing these results with the values for the

adhesion energy of the ZnO nanoparticles to the carbon foil (established using the AFM/Scratch test measurement) will allow to obtain fundamental data concerning the stability of ZnO coatings on graphite substrates.

3. The use of carbon foams impregnated with ZnO nanoparticles to store molecular mixtures of sugar alcohols will enhance the control of the PCM phase transition temperature and also the control of the transformation latent heat.

4. The thermal analysis methods will be used to perform a comparative study of the storing capacity of the macroporous carbon foams impregnated with sugar alcohols. This study will be helpful in the selection of the optimum storage systems.

5. The use of hydrothermal synthesis as a method for the PCM microencapsulation in core-shell composites.

References - selection

11. Heat and cold storage with PCM an up to date introduction into basics and applications, Mehling H., Cabeza L.F., 2008, XVI, 308p., 136 illus. Hardcover, ISBN 978-3-540-68556-2, Solid-liquid phase change materials – Springer 9783540685562-c1

64. R.M. PITICESCU et al., *Molecular and Liquid Crystals* 483 (2008) 216-227

65. M. Abrudeanu, R. R. Piticescu, R. M. Piticescu, *Sinteza pe cale umedă a pulberilor ceramice ultradisperse*, Editura tehnică, 1999.

84. D. Segal, *Chemical Synthesis of Advanced Ceramic Materials*, Cambridge Univ. Press (1989).

92. Adrian Mihail Motoc, Ioan Albert Tudor, Mirela Petriceanu, Viorel Badilita, Elena Palomo del Barrio, Prasanta Jana, Vanessa Fierro, Alain Celzard, Radu Robert Piticescu – *Materials Chemistry and Physics* 161 (2015) 219-227.

93. H. H. Al-Kayiem, S.C. Lin, A. Lukmon, *Nanoscience & Nanotechnology-Asia*, 2013, 3 (1), pp. 1-11

96. E. Celia, T. Darmanin, E.T. de Givenchy, S. Amigoni, F. Guittard, *J. Colloids and Interface Sci.* 2013, 402, pp. 1-18

101. T. Hamada, E. Fujii, D. Chu, K. Kato, Y. Masuda, *J. Crystal Growth* 2011, 314, pp. 180-184

103. K. Byrappa, M. Yoshimura, *Handbook of Hydrothermal Technology*, 2013, Chapter 1, pp. 1-49, Elsevier, ISBN: 978-0-12-375090-7

106. A. Bragaru, M. Kusko, E. Vasile, M. Simion, M. Danila, T. Ignat, I. Mihalache, R. Pascu, F. Craciunoiu, *Nanopart. Res.* 2013, 15, 1352-1367, DOI 10.1007/s11051-012-1352-0.

119. P. W. Atkins, *Tratat de Chimie Fizică*, Editura Tehnică, 1996.