Smart Energy and Sustainable Environment

2020, *23*(1): 5-12, https://doi.org/10.46390/j.smensuen.23120.76

PREPARATION OF THE Ni DOPED CARBON NANOFIBERS SYNTHESIZED BY ELECTROSPINNING

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Abstract:

Carbon nanofibers are very stiff, strong and light materials composed from tightly packed layers of graphite sheets stacked parallel one near the other in a regular pattern and aligned along the fiber axis. This study presents a facile approach to prepare composite Ni/C nanofibers through electrospinning of polymer solution. A mixed solution of polyacrylonitrile (PAN) in dimethylformamide (DMF) solvent along with $Ni(CH_3COO)_2$ was the precursor solution used to obtain composite Ni/C nanofibers. The amount of Ni salt was varied in order to study the influence of Ni percent on the composite fibers properties, particularly the pores dimension and the specific surface area. The composition and the structure of materials were investigated through elemental analysis and scanning electron microscopy (SEM). In addition, thermal gravimetric analysis (TGA) was performed to complete the composition study and the thermal degradation profile.

Article info:

Received 11February 2020
Received in revised form 24 February 2020
Accepted 28 February 2020
Available online 06 March 2020

Keywords*:*
Composite carbon nanofibers, electrospinning, specific surface area, electrocatalyst.

How to cite: Petreanu, I., Sisu, C., Soare, A., Andrei, R. D., Capris, C., Marinoiu, A. (2020). Preparation of the Ni doped carbon nanofibers synthesized by electrospinning. *Smart Energy and Sustainable Environment*, *23*(1), 5-12.

1. INTRODUCTION

Carbon fibers (CF) are composed mainly of carbon atoms, above 92 wt%, forming a crystal structure oriented in a large extent along the fiber direction. The atomic structure is similar to that of graphite, with flat sheets of carbon atoms in a regular hexagonal pattern. The differences consist in the way that the sheets are linked between them (Huang, 2009; https://carbosystem.com/en/carbon-fiber-3).

The manufacturing process involves two stages: the first stage consists in electrospinning the polymer solution or melt followed, in the second stage by a thermal treatment of the fibers obtained in the first stage. The precursor fibers obtained are stabilized in air at temperature between 200-400°C by an oxidative process. During stabilization, PAN

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molecules are crosslinked and cyclized via nitrile -C≡N groups suffering cyclization, dehydrogenation and finally oxidation, results an infusible, ladder-like structure.

Furthermore, at temperature between 900-1500°C in an inert atmosphere the heteroatoms are released yielding a structure with carbon content around 90 % and a turbostratic morphology. (Cao et al., 2017; Alarifi et al., 2018)

The molecular alignment of graphitic planes occurs when amorphous PAN solution is spuned in precursor fibers during electrospinning of polymer solution, due to shear forces, and keeps on during carbonization and graphitization processes. The smaller turbostratic crystallites give a higher tensile strength to PAN carbon fibers. Increasing the temperature treatment up to 2000-3000°C will bring a better alignment of graphitic structure, will increase the elastic modulus. Thus, mechanical behaviors of the carbon fibers depend on the final temperature in the thermal treatment: the maximum strength is provided by heating fibers at temperature up to 1500-1600°C while the elastic modulus still increase with temperature, up to around 3000°C.

Also, the electrical and thermal properties of carbon fibers vary widely depending on their structure. A high degree of crystallinity generally results in low electrical resistivity and high thermal conductivity. The porosity has a major effect on the electrical and thermal properties, so the resistivity increases exponentially as the specific surface area increase. It was notice if the volume of meso and macropores increase the resistivity of material increase. (Chen, 2016)

The carbon fibers (CF) are used as support for metal nanoparticles (Co, Ni or Fe) which serve as catalysts. CF obtained by carbonization of electrospun polyacrylonitrile (PAN), generally show high macroporosity (85%), high temperature resistance and good electrical and thermal conductivities. For this reason they can be used as catalyst carriers, electrochemical probes, energy storage electrodes, supercapacitors, high temperature filters or absorbents. (Bosch-Jimeneza et al., 2017)

Moreover, the carbon nanocomposites are used in various applications such as energy conversion and storage, capacitive deionization, catalysis, adsorption/separation, or in the field of biomedicine. One of the most studied methods for preparation of metal oxide-supported carbon fiber composites are electrospinning from solution. The carbon nanocomposites various synthetic routes were developed to achieve porous carbon nanofibers (CNF) composites with high surface area and tunable pore size distribution. Most of the preparation methods involve carbonization process at elevated temperatures of typically above 1200°C. So far, various metal or metal oxide nanoparticle (Pd, Pt, Ti, Ag, Au, Cu, Ni, Zn, and Ru) - supported CNF nanocomposites were reported. (Gopiraman & Kim, 2019) Due to the excellent properties such as high surface area, conductivity, and porosity, the CF-based nanocomposites are widely used for the energy applications such as energy storage systems (ESS) for clean and sustainable energy. Mainly three types of devices are very important and most commercialized energy storage systems such as batteries, electrochemical capacitors (ECs), and fuel cells. (Niu et al., 2019)

The purpose of this study is to develop a simple and effective method for preparation of new catalysts for Proton Exchange Membrane Fuel Cells (PEMFC). There are two aspects in this work, less studied in the preparation of catalyst for in PEMFC: use the carbon fibers as support for metal and the procedure to obtain the metal on carbon fibers support in the one step, from only one solution.

Mainly, we synthesized composite Ni/C nanofibers through electrospinning procedure. A mixed solution of polyacrylonitrile (PAN) in dimethylformamide (DMF) along with a Ni salt, $Ni(CH_3COO)_2$ was prepared in order to obtain the composite Ni/C nanofibers by electrospinning approach. Several concentrations of Ni salt into the polymer solution were used for studying the influence of the Ni amount on the nanocomposite Ni/C nanofibers properties, particularly the pores diameter and the surface area. The thermal decomposition was studied by

thermal gravimetric analysis (TGA); the composition was investigated by elemental analysis and the structure of materials by scanning electron microscopy (SEM).

2. EXPERIMENTAL

Polyacrylonitrile is well known as carbon fibers precursor. The structure of polymer, with repetitive vinyl cyanide structural units provides the ability to form interchains connections resulting a plane honeycomb structure (Fig.1).

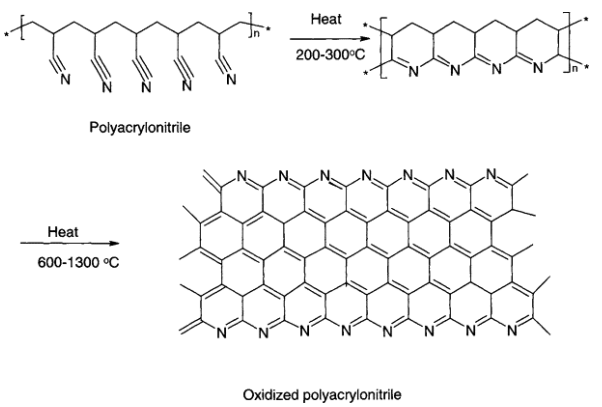

Figure 1. Synthesis of carbon honeycomb like structure from polyacrylonitrile, by thermal treatment (Hao, 2005)

Materials used for composite carbon nanofibers synthesis were:

- Polyacrylonitrile (PAN) with average molecular weight Mw = 150 000 g/mol, from Sigma-Aldrich, Germany;
- N, N-Dimethylformamide (DMF), 99%, from Alfa Aesar, Germany;
- Nikel (II) acetate (Ni(II)Ac) tetrahydrate, 99% from Merk.

The method used for preparation of the composite carbon nanofiber comprises following stages:

- Preparation of mixed solution for electrospinning;
- Forming the precursor fibers by electrospinning;
- Thermal annealing at temperature between 200-300°C under oxygen atmosphere for PAN chain cycling via nitrile groups;
- Continuous heating of fibers up to 1300°C or more, in order to obtain carbon nanofibers with controlled nitrogen and hydrogen contents having different properties (conductivities and dielectric constants).

In the first step, a solution containing 8 Wt% PAN into DMF was prepared. The solution was homogenized into the ultrasonic bath for 4.5 hours at 70°C. Furthermore, a determined amount of metallic salt, $Ni(CH_3COO)_2$ was added and mixed again on the ultrasonic bath, for another two hours, at 70°C. The amount of $Ni(CH_3COO)_2$ was varied (four different amount – see table 1) in the same composition of PAN/DMF solution obtaining four different mixtures.

The mixed solutions were electrospun one at a time resulting four different precursor fibers. These fibers were thermal treated and carbonized up to 1400°C. Four nanocomposite Ni/C nanofibers with various amount of Ni were obtained (table 1).

Characterization of the four samples of nanocomposite Ni/C fibers comprises the following analysis: elemental analysis, thermal gravimetric analysis (TGA), Scanning Electron Microscopy (SEM) and determination of the specific surface area and the pores dimension distribution by nitrogen adsorption/desorption method (BET method).

Chemical composition of nanocomposite carbon fibers was determined by elemental analysis with an elemental analyzer Flash 2000 from ThermoScientific (UK). Sample around 1-3 mg was placed into tin crucible and burned at 950°C. The resulted gases were separated on a Porapack separation column warmed up to 70°C. The oxygen percent in the samples was determined after the samples placed into the silver crucible was pyrolyzed at 1050°C. The resulted gas was fractioned on the SM5A column (with molecular sieves) and analyzed on a TC detector.

The microstructure of samples was studied through Scanning Electron Microscopy using a Sigma VP FEG Carl Zeiss device. Samples were placed on the carbonaceous support and scanned in liquid nitrogen atmosphere.

Thermal decomposition of nanocomposite Ni/C fiber samples was recorded on a TGA-DSC – NETZCH PROTEUS 80 analytical system. Each sample, about 27 mg weights, was heated in ramp, from ambient to 850°C with heating rate of 5°C/min in an inert atmosphere (argon).

For specific surface area determination it was used BET method (Brunauer, Emmett and Teller) which estimate surface area function of nitrogen sorption measurement. This measurements used a QuantachromeAutosorb IQ equipment from Quantachrome Instruments, US. Nitrogen sorption/desorption experiments proceed at 77 K (-196°C) temperature, after the samples were previously degassed for four hours at 115°C.

3. RESULTS AND DISCUSSIONS

Both *elemental analysis* and *thermal gravimetric* analysis provide information about chemical composition of samples: the elemental analysis determines weight percent amounts of C, N, H and O into the samples meanwhile thermal gravimetry give information about Ni amount, whose values are proportionally with final residues obtained after thermal degradation above 850°C. The comparative results are presented in table 1, along with the composition of initial solution, prepared for electrospinning.

Graphical representations of thermal decomposition of all samples have the same shape as that of the sample 4 (Fig. 2), with a small step of mass loss up to 600°C and the main thermal degradation above this temperature, probable due to most of nitrogen and hydrogen lost. The residual mass at final temperature, 850°C, increased in order of increasing Ni salt and it is proportionally to Ni amount in the sample (residual mass in table 1).

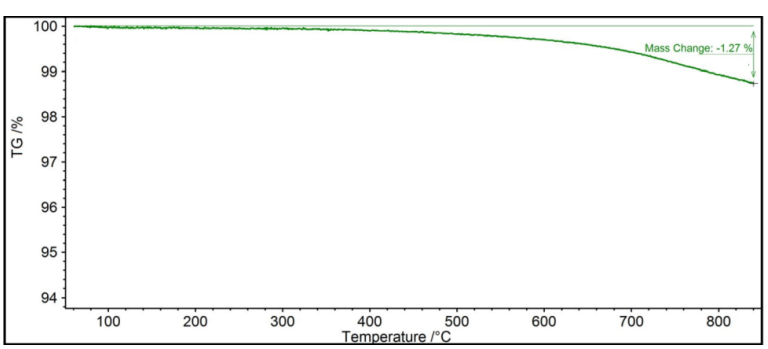

Figure 2. Thermal degradation of Ni/C composite carbon fibers (S_4)

Table 1. *Elemental composition and final residues of nanocomposite Ni/C carbon fibers*

Sample	Amount of Ni salt	Elemental analysis results wt %				Residual mass (850°C) wt%
		C	N	H	O	
S_1	0.0373 g	94.90	4.82	0.13	0.12	99.58
S_2	0.0746 g	95.33	4.37	0.12	0.11	99.32
S_3	0.1119 g	95.36	4.21	0.12	0.1	98.95
S_4	0.1492 g	95.52	3.87	0.12	0.14	98.73

The porous structure of composite carbon nanofibers presented in the *Scanning Electron Microscopy* images (Fig. 3) show inhomogeneous Ni particle distributions. The a), b) and c) images represent the micrographs of S_1 sample, the d), e), f) are the micrographs of S_2, g), h), i) are the images of sample S_3 and j), k), l) show the micrographs of S_4 at different magnifications. Increasing the magnification offers more details of sample structure, thus a), d), g) and even j) images reveal the fibrous morphology of the four samples. In the b), e), h), k) images from Fig. 3, on notice the porous structure of the fiber samples. Distribution of Ni particles, more or less uniformly is highlighted at high magnification (c), f), i), l), Fig. 3).

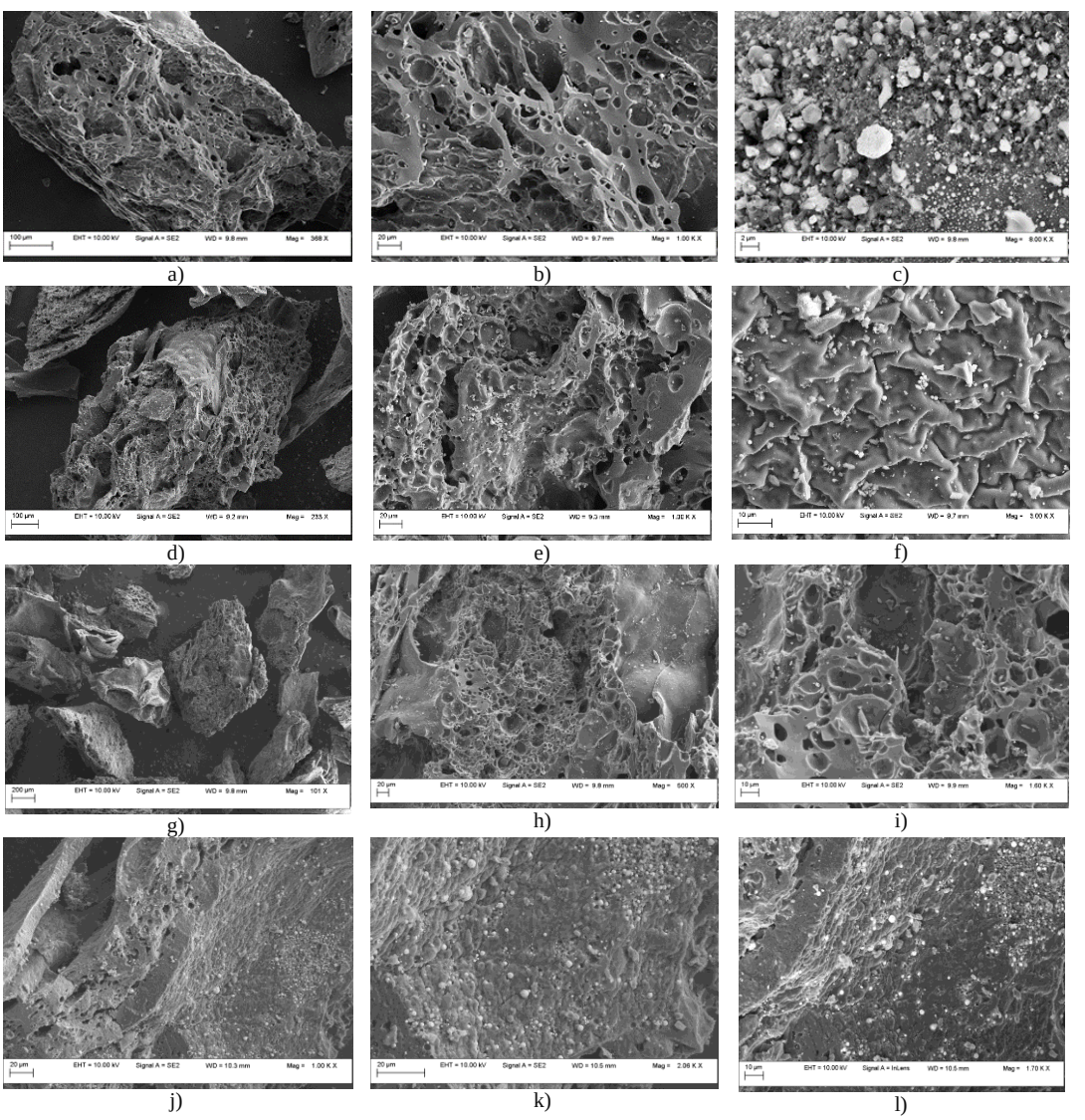

Figure 3. SEM images of composite Ni/C carbon fibers at different resolution show: a fragment of carbon fiber (a, d, g, j); porous structure of carbon fiber (b, e, h, k) and Ni particles distribution (c, f, i, l), inside or on the surface of fibers

The analysis of the dates obtained by *nitrogen absorption/desorption* on porous samples makes it possible calculation of specific surface area through the BET method. Also, the pore diameters and the pore size distribution can be estimated using Barrett

Joyner Halenda (BJH) method. The values of specific surface area and pore size of the samples, determined using the two methods (BET and BJH) are presented in table 2. Graphic representations of the volume of nitrogen function of relative pressure, during the absorption/desorption isotherm cycles are displayed in fig. 4. Also, the pore size distributions are shown in fig. 5.

Table 2. *Specific surface area and pore size for composite carbon nanofibers obtained by electrospinning (Ni/C_{el}) noted also S_1-S_4*

Sample	Surface area (BET) m^2/g	Surface area (BJT) m^2/g	Pore diameter (BJT) nm	Pore volume (BJT) cm^3/g	Corr. Coef. (BET)
S_1	6.28	3.75	3.9	0.005	0.999146
S_2	22.52	12.42	3.7	0.020	0.999162
S_3	14.23	20.52	3.7	0.029	0.999042
S_4	52.30	34.75	3.9	0.039	0.999224

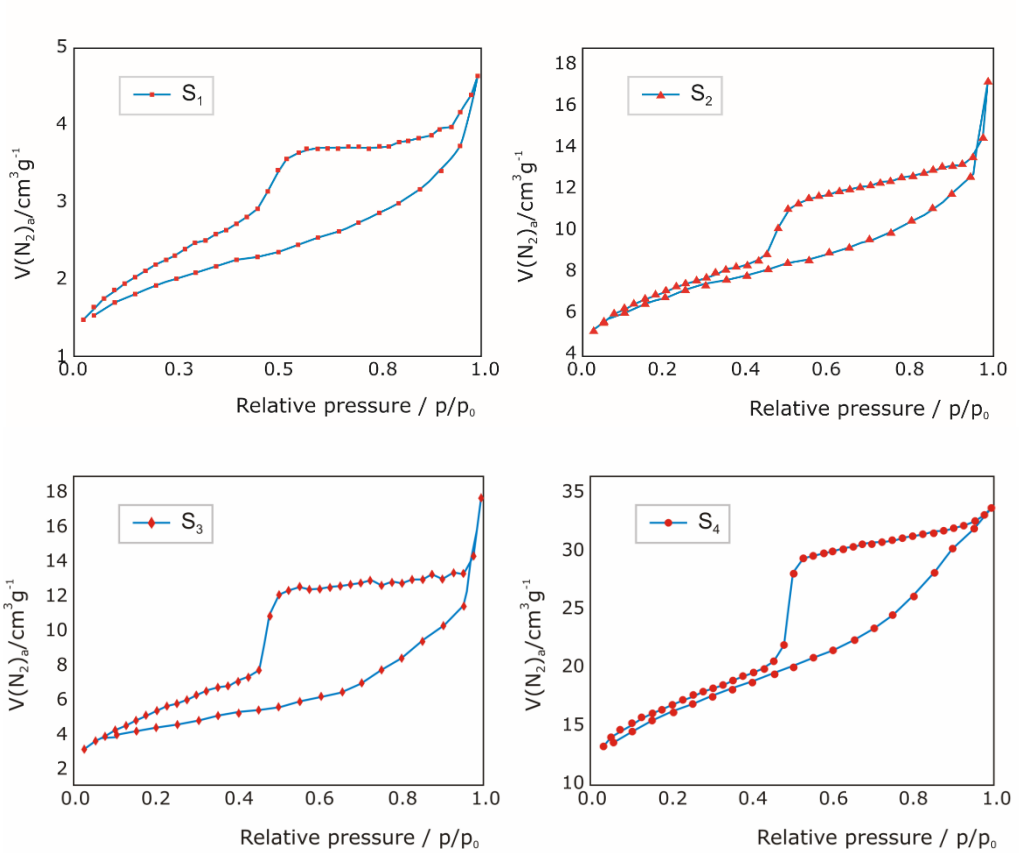

Figure 4. Nitrogen absorption/desorption isotherms on the four composite Ni/C carbon samples

The shape of absorption/desorption isotherms are the same for all samples, type IV isotherm (according to IUPAC classification) with a hysteresis loop associated with capillary condensation taking place in mesopores and a limiting uptake at high p/p_o values. One notices a steep adsorption at low relative pressure indicating presence of considerably micropores density (Sing, 1982). The absorption volume is also increased in the high relative pressure which confirmed the presence of mesopores. Additionally, the hysteresis loop corresponds to H1 type (IUPAC classification) suggests morphology consist in

aggregate of flat sheet particles, accordingly with literature description and SEM images of electrospun carbon fibers. The irregular porous system was formed during electrospinning and thermal annealing.

Characteristic features of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high p/p°. The initial part of the Type IV isotherm is attributed to monolayer/multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form (Sing, 1982).

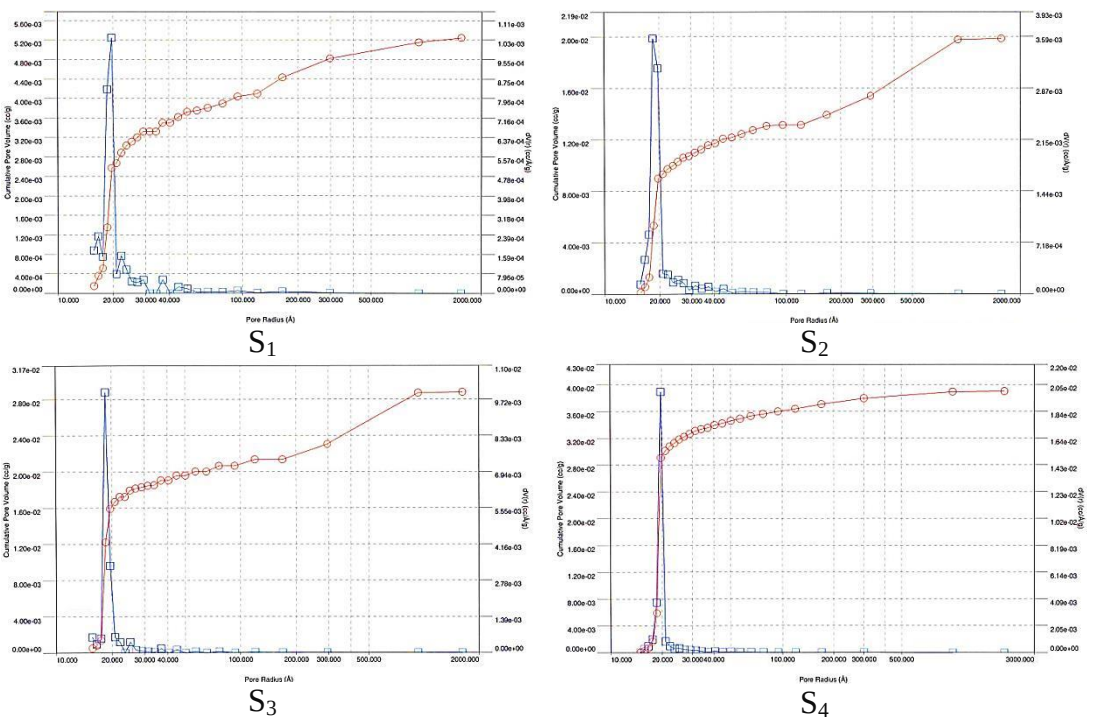

Figure 5. Pore size distribution and volume of absorbed gas for the four composite porous carbon samples

4. CONCLUSIONS

Composite Ni/C carbon fibers with mesoporous structure were obtained through electrospinning method. The nickel acetate (Ni precursor) was mixed into polyacrylonitrile solution in dimethylformamide and the mixture was electrospun using a dedicated device. The obtained fibers were thermal treated up to 1400°C resulting mesoporous composite carbon fibers.

Four amount of Ni salt in ascending order were used in order to obtain different percent of Ni in carbon fibers. The presence of Ni can be noticed in the SEM images. The increased values of residual mass obtained after thermal decomposition (TGA) validate the increased amount of Ni in carbon fibers corresponding to increasing amount of Ni salt into initial solution (table 1).

The specific surface area (BJH) and the pore volume increased with the amount of Ni in the carbon fibers. The same trend exhibited the BET value of surface area excepting S_3. The average pores diameters are between 3.7-3.9 nm (tables 2), in the range of mesopores.

This work confirms the possibility to obtain nanocomposite carbon fibers through a relative easy and cheap method, with controlled porosity and metal content.

Acknowledgement: The authors wish to thank Ms. Elena Marin for BET measurement.

Funding: This work is supported by the Ministry of Research and Innovation from Romania, Project PN 19 11 02 01.

Author Contributions: Conceptualization, Adriana Marinoiu; methodology, software, C.C.; validation, Adriana Marinoiu; investigation, Radu Dorin Andrei,Irina Petreanu, Amalia Soare,. Claudia Sisu,and Adriana Marinoiu; writing—original draft preparation, writing—review and editing Irina Petreanu.

Conflict of Interest Statement:

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