

INFLUENCE OF THE SUPPORT ON THE MORPHOLOGY OF Co-Sn, Ni-Sn, Co-Ni NANOPARTICLES SYNTHESIZED THROUGH A BOROHYDRIDE REDUCTION METHOD APPLYING A TEMPLATE TECHNIQUE

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Abstract. Intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles have been synthesized through a borohydride reduction with NaBH₄ in aqueous solutions of the chloride salts of Co, Ni, Sn at room temperature using a template technique with a carbon support. As a result nanocomposite materials have been obtained in situ. The ratio of the metallic components has been chosen according the phase diagrams of the relevant binary (Co-Sn, Ni-Sn, Co-Ni) systems: Co:Sn=35:65, Ni:Sn=45:55, Co:Ni=50:50. As carbon supports have been used graphite and carbon powder. To avoid the nanoparticle's aggregation β-cyclodextrin has been added to the reaction solutions. To study the influence of the supports used on the morphology, specific surface area, elemental and phase composition of the synthesized intermetallic nanoparticles and their carbon nanocomposites SEM, EDS, BET, and XRD investigation techniques have been used. The particle's morphology varies with the different supports, but in the all cases it is typical for alloyed materials. The nanoparticles are different in shape and size and exhibit a tendency to aggregate. The last-one is due to the unsaturated nanoparticle's surface and the existing magnetic forces. Regardless of the elemental composition, the nanosized particles are characterized by a relatively high specific surface area (SSA). The Ni-Sn nanoparticle have the largest SSA (80 m²/g), while the Co-Sn particles have the lowest SSA (69 m²/g). The use of a carrier modifies the SSA of the resulting nanocomposites differently depending on the size and shape of the carrier's particles. The studies conducted on the intermetallic nanoparticles synthesized with various carriers demonstrate that the particle's morphology, size, and specific surface area for the different supports are suitable for use as catalysts, electrode materials in Li-ion batteries and as magnetic materials for biomedical applications.

1. INTRODUCTION

Nowadays there is a high demand for modern high tech and nanotechnology to meet the worldwide needs of three-dimensional structures, nanomaterials, masking materials for military power, energy materials, eco-materials, and functional materials [1-14].

In recent years, research has been focused on the synthesis of various metal alloys and intermetallic compounds based on tin (Sn), antimony

(Sb) and silicon (Si), mainly because of their potential use as alternative electrode materials in Li-ion batteries. The requirements for high specific capacity of the electrode material and maintaining high cycling can not be fulfilled by pure Sn, Sb, and Si [1]. During charge-discharge cycles their volume changes significantly causing cracking or destruction of the electrode. Therefore, in the commercial production of batteries, their use was not established.

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Many studies have been focused on creating composites based on carbon materials and intermetallic nanoparticles. The combination of the unique properties of carbon and intermetallic (Cu-Sn, Co-Sn, Ni-Sn, Co-Ni) nanoparticles makes carbon nanocomposites on their basis promising materials for a new generation of electrodes in modern energy storage systems [1-14].

Intermetallic nanoparticles as an important component of the electrode composite materials can be obtained by various methods.

Reductive precipitation is a well-known technique in materials chemistry and has been used to synthesize metal, alloyed and intermetallic powders, mainly for Li-ion batteries applications. This method represents an interesting "bottom-up" alternative to the mechanical "top-down" grinding and alloying by ball-milling. Ultrafine powders can be prepared, as well as the particle size and the morphology of the precipitated materials can be controlled by several parameters (i.e. precursor concentrations, temperature, complexing agents). Chemical reduction is a relatively simple experimental procedure, but there are some disadvantages associated with obtaining large size particles (up to several hundreds of nanometers) and the formation of oxides (hydroxides) on the nanoparticle's surface. In order to control the growth of the reduced particles, capping agents such as polyvinylpyrrolidone (PVP), β -cyclodextrin have been widely used. The polymer molecules attach to the metallic nucleus, thereby reducing the surface energy and preventing further agglomeration [2-5].

The reductive precipitation of metal salts in aqueous solutions using sodium borohydride (NaBH_4), potassium borohydride (KBH_4), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) at room temperature is a versatile and effective technique to synthesize bimetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles at different mass ratios between the metallic components implementing template synthesis with a carbon support [3-8]. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is added to the mixture of the metal ions as a complex agent, also trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and ammonia are used to adjust the pH value.

The reductive precipitation can be carried out also in organic solutions (such as a polyalcohol, mainly ethylene glycol) of the relevant metallic salts to prepare bimetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles. This polyol method allows achieving an effective control on the particle size and size distribution [3]. The polyalcohol serves as solvent and reducing agent, as well as the nucleation and growth processes of nanoparticles are controlled by the tem-

perature. Thus prepared nanoparticles have an amorphous structure and are relatively small in size up to 10 nm, however the resulting elemental composition may differ from that initiated with the starting precursor.

In summary, amorphous intermetallic nanoparticles have been prepared by dissolving metal precursor salts in water or alcohol, mixing with a complexing agent, and reduction solution [3-8]. As-synthesized nanoparticles have been characterized using XRD, SEM, EDS, TEM, BET, Raman spectroscopy, and FTIR analysis.

Composites based on intermetallic nanoparticles with a different carbon matrix have also been synthesized. Sn-Co-graphene composites are obtained through a co-precipitation method in solution of citric acid, $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, and graphene oxide with NaBH_4 as a reducing agent [9]. The obtained Sn-Co nanoparticles are homogeneously attached to the surface of graphene. These composites are evaluated by cyclic voltammetry and galvanostatic charge-discharge tests to be used in Li-ion batteries. The prepared composites exhibit high reversible capacity with excellent cyclic stability. This electrochemical behavior could be ascribed to the positive synergistic effect of the combination of the buffering effects of cobalt and the excellent conductivity of graphene, which could restrain the volume variation, keep the structure stable, and increase the conductivity of the whole system.

A sonochemical method has been also used to prepare composite electrode materials based on intermetallic nanoparticles and polyacrylonitrile (PAN) [10]. Due to the ultrasound irradiation applied small particle's size is achieved. After annealing at 490 °C under Ar-flow, the polymer PAN is partially carbonized and the metallic nanoparticles are surrounded by a carbonaceous matrix. The main metallic phase is CoSn_2 . The resulting CoSn_2 -C composites show improved electrochemical behavior in comparison with the pure crystalline CoSn_2 . The aggregation of the nanosized metallic particles during the electrochemical cycling is suppressed by the carbonaceous matrix (pyrolytic PAN).

In the last few decades the research of alternative anode materials for high-power and high-density lithium ion batteries is one of the most widely investigated topics in materials chemistry. CoSn_3 -MWCNTs nanohybrids have been successfully obtained via a chemical reduction method in a polyol system assembling CoSn_3 nanoparticles on noncovalently poly(diallyldimethylammonium chloride)-functionalized multiwalled carbon nanotubes (MWCNTs) [11]. The as-synthesized CoSn_3 -

MWCNTs nanohybrids have been applied as anodes in lithium-ion batteries and show better lithium storage performance compared to the bare CoSn_3 nanoparticles and MWCNTs. The MWCNTs prevents the agglomeration and improve the electronic conductivity of the active material resulting the enhanced cyclic performance.

Fine metallic (Co, Sn) and alloyed (Co–Sn) powders are prepared by reductive precipitation (RP) with electrostatic spray pyrolysis (ESP) to be used as alternative anode materials for rechargeable Li-ion batteries [12]. This technique combines aerosol generation by electric means together with chemical precipitation in order to form solid particles with tunable features. This synthesis method called electrostatic spray reductive precipitation (ESRP) represents a new route to produce metal, alloyed and intermetallic particles. The coupling these two physical (ESP) /chemical (RP) techniques enables the formation of solid nanoparticles finely dispersed into a liquid medium preventing the particle agglomeration during the reaction process.

Among the available methods to synthesize intermetallic (Sn–Ni, Co–Sn) nanoparticles, the electrochemical deposition process has several advantages such as a control of the thickness, morphology and composition of the deposited films by adjusting the operating conditions [13]. In addition, the films electrodeposited onto a substrate can be used directly as electrode materials without any binder. Usually, tin alloys used as anode material in Li battery are electrodeposited in aqueous solutions but it requires in most of cases a further annealing at moderate or high temperature. H. Groult et al. proposed a new electrochemical route for the synthesis of tin-based alloys in molten salts [14]. Ni–Sn and Co–Sn alloys are prepared by electroreduction of Ni(II) or Co(II) and Sn(II) ions in molten chloride LiCl–KCl salts giving rise to Sn-based alloys with a well-defined composition. This approach allows the preparation of Ni–Sn and Co–Sn alloys with different compositions depending on the operating conditions, without any further ex situ heat treatment as it is usually applied according to literature.

The critical analysis of the literature suggests that studies have been focused on composite materials for electrodes based on intermetallic nanoparticles compounds (binary tin alloys M_xSn_y , where M is an inert component usually based on Cu, Co or Ni) and carbon matrices. As a carbon matrix, graphite is used to serve as a stabilizer of the electrode material, and as working electrode is involved in the processes of lithiation and delithiation.

Thus, it simultaneously increases the capacity and mechanical resistance of the electrode material.

This literature review related to the synthesis of metallic/intermetallic nanoparticles and their unique properties motivated us to synthesize intermetallic Co–Sn, Ni–Sn, Co–Ni nanoparticles via chemical reduction method using NaBH_4 as a reducing agent and apply at the same time a template technique with a carbon support. The aim of this paper is to study the influence of different carbon supports used during the template synthesis on the morphology, specific surface area, elemental and phase composition of the as-synthesized and template synthesized intermetallic nanoparticles (respectively in situ obtained carbon nanocomposites) at a mass ratio between the metallic components chosen according the phase diagrams of the relevant binary (Co–Sn, Ni–Sn, Co–Ni) systems.

2. EXPERIMENTAL SET-UP

Borohydride reduction method with NaBH_4 in a mixture of aqueous solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salts is used to synthesize intermetallic Co–Sn, Ni–Sn, and Co–Ni nanoparticles. The ratios of the metallic components have been chosen according to the phase diagrams of the respective binary systems (Co:Sn=35:65, Ni:Sn=45:55, and Co:Ni=50:50). To reach the relevant ratio Co:Sn=35:65 we used 35 ml 0.1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 65 ml 0.1 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, respectively for a ratio Ni:Sn=45:55 – 45 ml 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 55 ml 0.1 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and for a ratio Co:Ni=50:50 – 50 ml $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 50 ml 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. In the all cases the quantity of the reducing agent stabilized with NaOH is 100 ml 0.2 M NaBH_4 to fully complete the reduction process. For each experimental condition 0.44 g citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is added as a stabilizing ligand.

The synthesis is carried out in a double-wall cell to keep a constant temperature (by a thermostat) ensuring a consecutively introducing of the initial solutions and continuously mechanical stirring of the reaction mixture with a magnetic stirrer. The experiments are run at room temperature and atmospheric pressure. The reduction process is completed in 2 minutes adding the reducing agent drop wise. Fine powder precipitates are obtained. They are filtrated, washed with a distillate water and alcohol and dried in a vacuum oven for 24 hours at 100 °C.

Intermetallic Co–Sn, Ni–Sn, and Co–Ni nanoparticles are synthesized through the same borohydride reduction method using template tech-

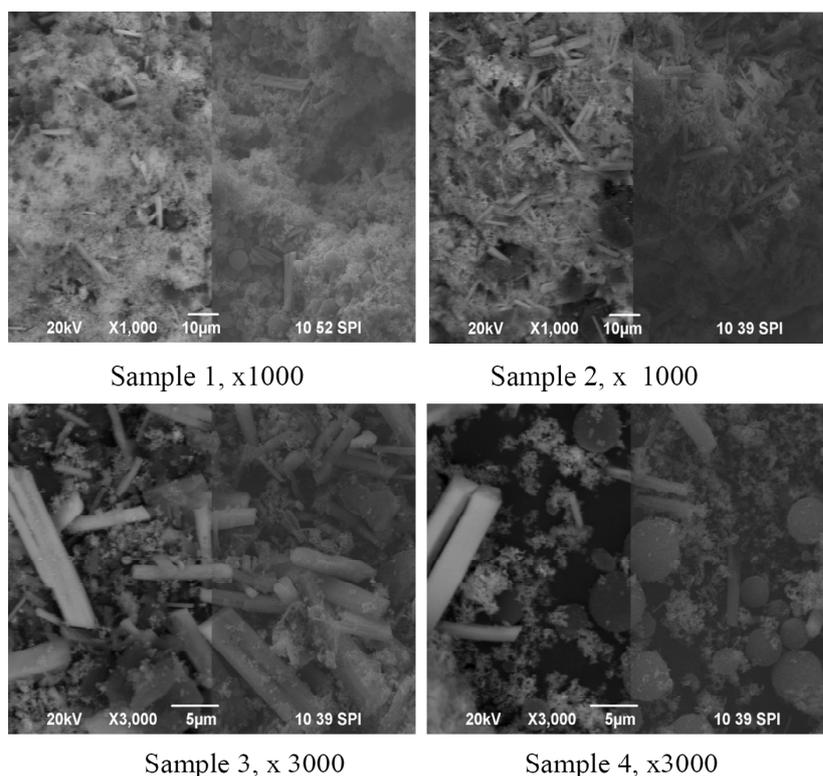


Fig. 1. SEM images of the samples synthesized at a ratio Co:Sn=35:65: Sample 1-Co-Sn nanoparticles, Sample 2-Co-Sn nanoparticles/CF, Sample 3-Co-Sn nanoparticles/CF and β -CDx, Sample 4-Co-Sn nanoparticles/C-powder.

nique with a carbon support at the same technological conditions as described above (the same concentrations and quantities of the reaction solutions and reducing agent solution, the same ratio of the metallic components).

As supports are used a fluorinated graphite (CF), CF in the presence of β -cyclodextrin (β -CDx) and carbon-powder (C-powder). This way carbon nanocomposites are obtained in-situ. β -cyclodextrin is used as a capping agent to prevent the nanoparticles aggregation decreasing their surface energy and improve the nanoparticles dispersion. The used quantities of CF, β -CDx, and C-powder are respectively 0.36 g/100 ml. The ratios are respectively 20% support (CF or C-powder): 80% intermetallic (Co-Sn, Ni-Sn, and Co-Ni) nanoparticles and also 20% CF: 20% β -CDx: 60% intermetallic (Co-Sn, Ni-Sn, and Co-Ni) nanoparticles.

The morphology of the synthesized Co-Sn, Ni-Sn, and Co-Ni nanoparticles and their carbon nanocomposites is studied with Scanning electron microscopy (SEM). The SEM images are made with a JEOL JSM 6390F (Japan) SEM microscope at accelerating voltage of 20 kV in a combined regime (SPI image). The BET method is based on low temperature (77.4K) adsorption of nitrogen and is in-

tended to explain the multilayer physical adsorption of gas molecules on a solid surface. The measurement of the specific surface area based on the theory of Browneauer, Emmett and Taylor was performed with a Quantachrome Instruments NOVA 1200e (USA). The elemental dispersitive analysis (EDS) is made using the same SEM microscope with an appliance for Energy-dispersive X-ray spectroscopy. The phase composition of the investigated samples is determined by X-ray diffraction (XRD). The X-ray diffraction patterns of all samples are collected within the 2θ range from 10° to 95° with a constant step 0.03° and counting time 1 s/step on Philips PW 1050 diffractometer using $\text{CuK}\alpha$ radiation.

3. RESULTS AND DISCUSSION

3.1. SEM study of the morphology of the intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles synthesized through a borohydride reduction

Fig. 1 presents SEM images of the Co-Sn nanoparticles synthesized at a ratio Co:Sn=35:65 through a borohydride reduction and their carbon nanocomposites prepared through the same method

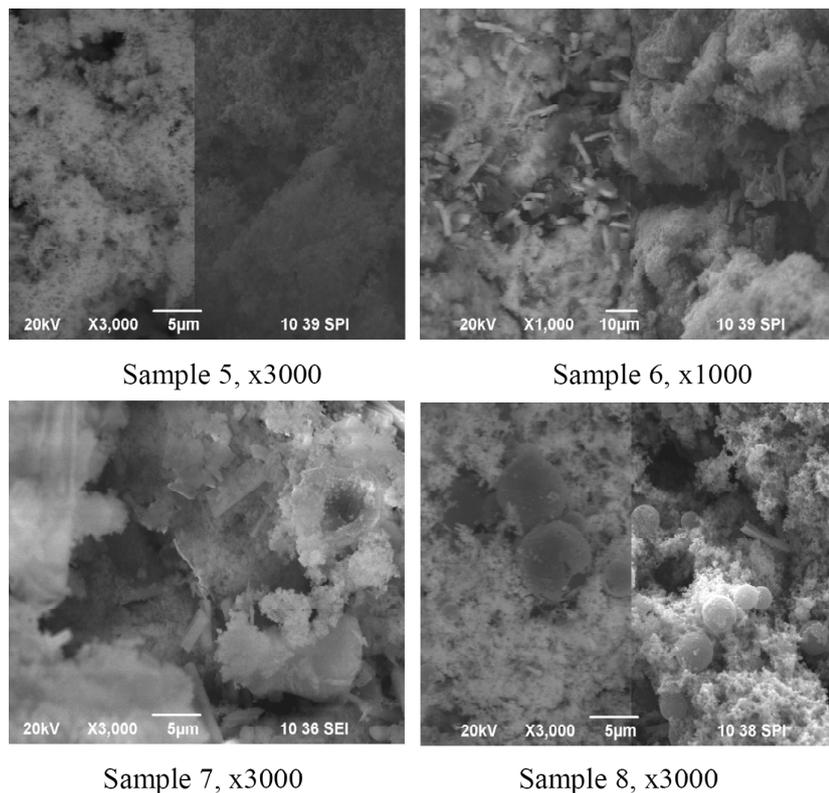


Fig. 2. SEM images at a different magnification of the samples synthesized at a ratio Ni:Sn=45:55: Sample 1-Ni-Sn nanoparticles, Sample 2-Ni-Sn nanoparticles/CF, Sample 3-Ni-Sn nanoparticles/CF and β -CDx, Sample 4-Ni-Sn nanoparticles/C-powder.

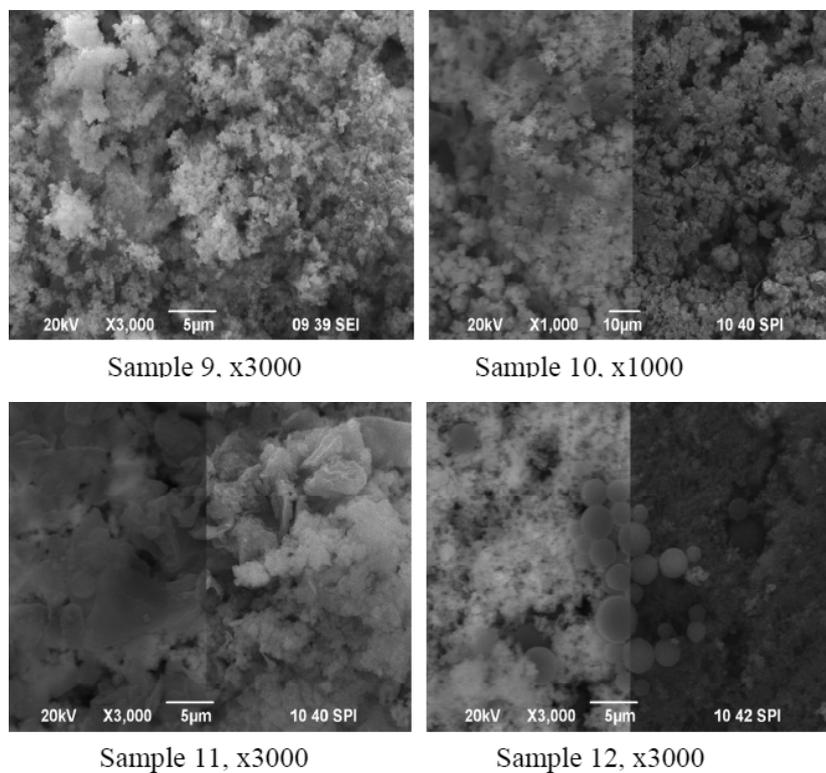


Fig. 3. SEM images at a different magnification of these samples synthesized at a ratio Co:Ni=50:50: Sample 1-Co:Ni nanoparticles, Sample 2-Co:Ni nanoparticles/CF, Sample 3-Co:Ni nanoparticles/CF and β -CDx, Sample 4-Co:Ni nanoparticles/C-powder.

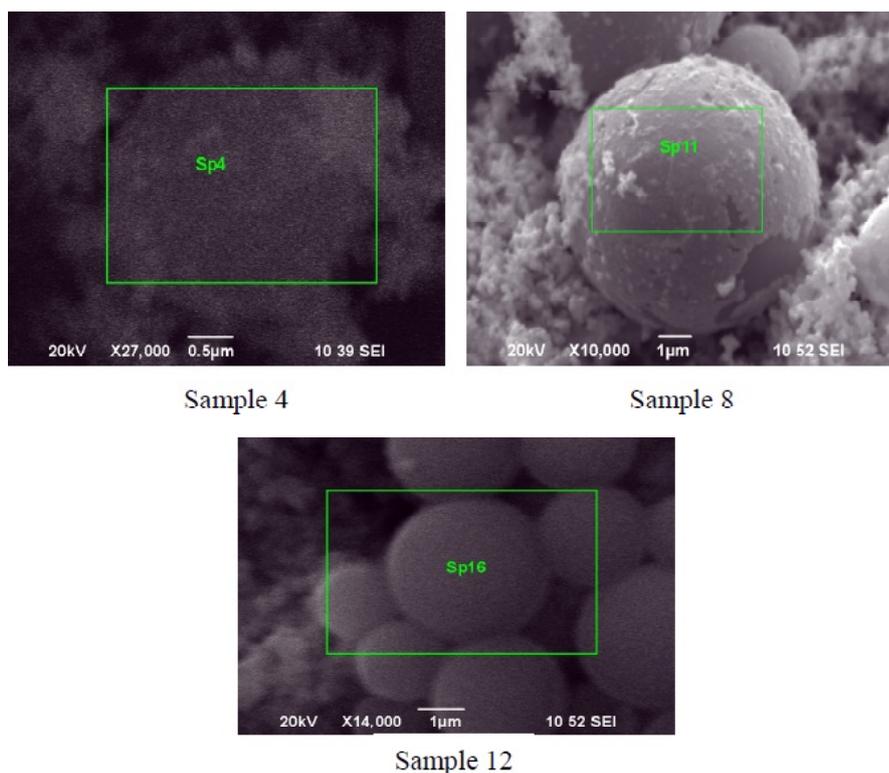


Fig. 4. SEM images of the samples synthesized with a carbon powder as a support: Sample 4-Co:Sn nanoparticles synthesized at a ratio Co:Sn=35:65, Sample 8-Ni-Sn nanoparticles synthesized at a ratio Ni:Sn=45:55, Sample 12-Co:Ni nanoparticles synthesized at a ratio Co:Ni=50:50.

by a template technique using a support, respectively CF, CF in the presence of β -CDx and C-powder. Fig. 2 demonstrates SEM images of the Ni-Sn nanoparticles synthesized at a ratio Ni:Sn=45:55 through the same borohydride reduction and their carbon nanocomposites prepared by a template technique using the same supports. Fig. 3 shows SEM images of the Co-Ni nanoparticles synthesized at the same experimental conditions at a ratio Co:Ni=50:50 and their carbon nanocomposites prepared the same way as the Co-Sn and Ni-Sn nanoparticles.

The SEM images of the Co-Sn nanoparticles and their carbon nanocomposites show a morphology typical of alloy materials. Particles with irregular shape and parallelepiped-shaped particles probably from Sn are observed. The particles are aggregated. When using graphite as a carrier characterized by a flaked structure, the synthesized particles with irregular shape are similar to the flake-like particles of graphite. In this case, the graphite carrier has influenced the formation of Co-Sn nanosized particles. It is noted that the particles tend also to aggregate, which is typical of the nanosized state. To overcome this undesirable effect in the synthesis, β -cyclodextrin, which is structurally a hollow sphere

with superficial functional groups, is used. It has to cover the particles and prevent their aggregation. In the case of a synthesis using carbon powder composed of spherical grains, Co-Sn nanosized particles are formed between these spherical carbon grains, which are at the same time evenly coated with a thin Co-Sn layer.

In Fig. 4 SEM images made at a different magnification in SPI regime of intermetallic nanoparticles synthesized with a carbon powder as a support are shown. Sample 4 presents Co:Sn nanoparticles template synthesized at a ratio Co:Sn=35:65, sample 8 presents Ni-Sn nanoparticles template synthesized at a ratio Ni:Sn=45:55, and sample 12 - Co-Ni nanoparticles template synthesized at a ratio Co:Ni=50:50.

It can be seen that the carbon powder grains are covered with relevant intermetallic uniform layer and also that the intermetallic nanoparticles are formed between the support grains. In these cases the carbon powder used as a carrier during the template synthesis influences the formation of the particles and especially their shape. Small spherical particles, which tend to aggregate less, are observed. It could be said that the carbon powder support is suitable for forming regular particles with spherical

shape. In the case of Co-Sn nanoparticles when graphite support is used particles irregular by shape and different in size are formed. When using graphite as a support, more aggregation of the nanoparticles is observed. In the case of Ni-Sn nanoparticles also using graphite support particles irregular by shape and different in size are formed as well. But in the case of Co-Ni nanoparticles very small almost the same in size particles are formed exhibiting an expressed tendency to aggregation. To avoid this undesirable effect β -cyclodextrin is used as a capping agent during the nanoparticle's synthesis. In the case of Co-Sn nanoparticles the β -cyclodextrin prevents the aggregation and single particles could be observed although they are different in shape and size (Fig. 1, sample 3). But in the case of Ni-Sn (Fig. 2, sample 7) and Co-Ni nanoparticles (Fig.3, sample 11) the β -CDx did not affect the aggregation – different size aggregates are observed.

It could be said that in all three cases of the obtained intermetallic nanoparticles when different supports are used during the synthesis the morphology is influenced in a different way. In regards to the formation of particles with low dispersion and similar size, the most suitable carrier is carbon powder.

According the literature the graphite used as a carbon matrix of the composites with intermetallic nanoparticles serves not only for stabilizing the electrode material, but also as working electrode is in-

involved in the processes of lithiation and delithiation. Thus, it simultaneously increases the capacity and mechanical resistance of the electrode material.

Our studies of the influence of the various carbon support used in the synthesis of intermetallic nanoparticles have shown that in terms of particle's morphology and particle's size, carbon powder is the most suitable carrier. We are going to perform electrochemical tests by a cyclic voltammetry and galvanostatic charge-discharge tests to determine the effect of the carbon powder matrix on the electrochemical behavior of the composite electrode materials based on a carbon powder and intermetallic nanoparticles.

We expect composite materials based on carbon matrix and Co-Sn and Ni-Co nanoparticles to be suitable electrode materials for lithium ion batteries, while Co-Ni nanoparticles and their carbon composites would likely exhibit good magnet properties suitable for use in biomedicine in the delivery of drugs for the treatment of cancer.

3.2. Results for the surface elemental composition from the EDS analysis of the investigated samples

Energy dispersive spectroscopy (EDS) analysis is used to determine the elemental composition of the nanoparticles. The results for the elemental com-

Table 1. EDS results for the elemental composition of the Co-Sn nanoparticles.

Sample	Element				
	Co mass%	Sn mass%	O mass%	C mass%	F mass%
S1	15.66	42.61	41.73	/	/
S2	18.65	36.16	23.10	16.4	5.69
S3	10.96	22.95	21.00	28.35	16.74
S4	8.64	26.61	25.86	38.89	/

Table 2. EDS results for the elemental composition of the Ni-Sn nanoparticles.

Sample	Element				
	Ni mass %	Sn mass%	O mass%	C mass%	F mass%
S5	24.04	42.63	33.33	/	/
S6	18.61	32.94	18.58	18.99	10.88
S7	11.26	22.23	28.75	24.93	12.84
S8	0.91	6.39	21.15	71.55	/

Table 3. EDS results for the elemental composition of the Co-Ni nanoparticles.

Sample	Element				
	Co mass%	Ni mass%	O mass%	C mass%	F mass%
S9	30.22	29.75	40.02	/	/
S10	7.07	7.24	41.37	35.56	8.75
S11	23.31	22.48	37.08	17.12	/
S12	1.37	1.21	18.65	78.77	/

Table 4. Experimental data for the specific surface area, SSA [m^2/g] measured by BET method.

Sample	Sample 1 Co-Sn	Sample 2 Co-Sn/CF	Sample 5 Ni-Sn	Sample 6 Ni-Sn/CF	Sample 9 Co-Ni	Sample 10 Co-Ni/CF
SSA, [m^2/g]	69	50	80	55	75	149

position from the EDS analysis are given in Tables 1-3.

The experimental data for the elemental composition on the nanoparticles show that in these three cases of the synthesized intermetallic nanoparticles the ratio of the respective metallic components (Co:Sn=35:65, Ni: Sn=45:55, Co: Ni=50:50), selected according to the phase diagrams of the relevant binary systems and set in the initial reaction solutions, is preserved with sufficient precision.

3.3. Results for the specific surface area, SSA [m^2/g], measured by BET method

The experimental data for the specific surface area, SSA [m^2/g], measured by BET method is given in Table 4.

Regardless of the elemental composition, samples representing nanoparticles and their carbon composites are characterized by a relatively large specific surface area, SSA [m^2/g]. The Ni-Sn particles have the highest SSA = 80 m^2/g , while the Co-Sn particles have the smallest SSA = 69 m^2/g . The Co-Ni particles have SSA = 75 m^2/g .

The nanocomposites based on Co-Sn and Ni-Sn particles synthesized with a carrier of graphite, have a smaller specific surface area than that of the particles: for composites with Co-Sn particles the SSA = 50 m^2/g , while for composites with Ni-Sn particles the SSA=55 m^2/g , which could be due to the larger particle size of the CF carrier. For nanocomposites with Co-Ni nanoparticles and graphite matrix, the specific surface area is greatest (SSA

= 149 m^2/g), which could be explained probably by the formation of small particles between the graphite flaked grains.

3.4. Study of the phase composition by XRD analysis of the synthesized intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles and their carbon-based nanocomposites

In Figs. 5a-5c XRD spectra of the synthesized intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles and their carbon nanocomposites are presented.

In Fig. 5a XRD spectra of sample 1 presenting Co-Sn nanoparticles synthesized at a ratio Co:Sn=35:65 and samples 2-4 presenting their carbon nanocomposites with a matrix respectively of CF, CF in the presence of β -CDx and carbon powder are shown. XRD analysis has proved the formation of two main phases: CoSn ($2\theta=28^\circ, 38^\circ, 42^\circ, 44^\circ, 52^\circ$) and CoSn_2 ($2\theta=32^\circ, 35^\circ$). In the case of the composites phases of Sn ($2\theta=31^\circ$) and carbon ($2\theta=45^\circ$) are also determined and impurity phases of CoO_2 ($2\theta=62^\circ$) and SnO_2 ($2\theta=26^\circ, 62^\circ, 76^\circ$) are specified.

In Fig. 5b XRD spectra of sample 5 presenting Ni-Sn nanoparticles synthesized at a ratio Ni:Sn=45:55 and samples 6-8 presenting their carbon nanocomposites with a matrix respectively of CF, CF in the presence of β -CDx and carbon powder are presented. XRD analysis has also proved the formation of two main phases: Ni_3Sn_4 ($2\theta=34^\circ, 42^\circ$) and Ni_3Sn ($2\theta=52^\circ, 60^\circ$), as well as phases of Ni ($2\theta=26^\circ$) and Sn ($2\theta=28^\circ$) and carbon ($2\theta=44^\circ$,

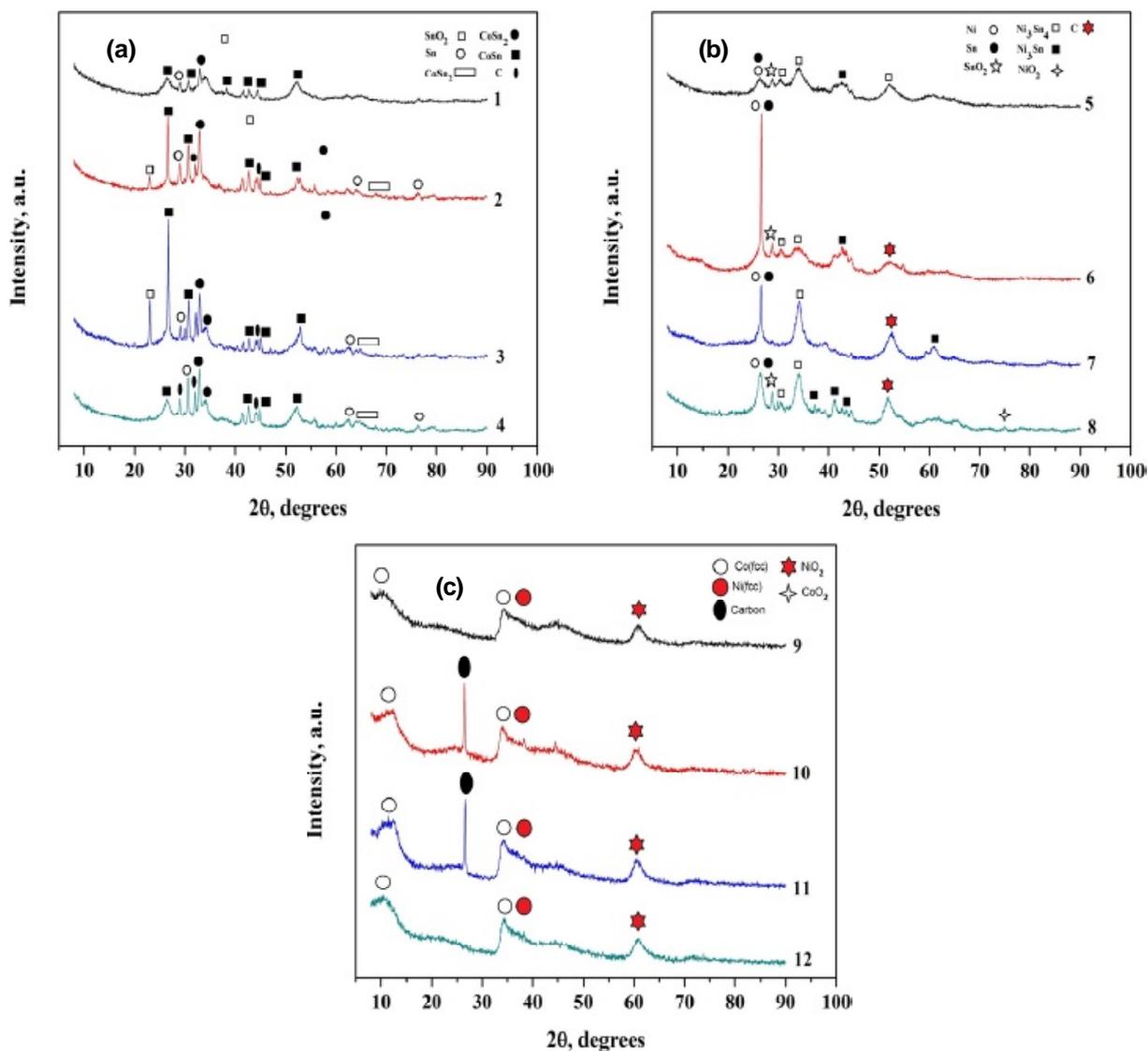


Fig. 5. XRD spectra of the investigated samples: a-Co-Sn nanoparticles/Co:Sn=35:65 (sample 1), Co-Sn/CF composite (sample 2), Co-Sn/CF/ β -CDx composite (sample 3), Co-Sn/C-powder composite (sample 4); b-Ni-Sn nanoparticles/Ni:Sn=45:55 (sample 5), Ni-Sn/CF composite (sample 6), Ni-Sn/CF/ β -CDx composite (sample 7), Ni-Sn/C-powder composite (sample 8); c-Co-Ni nanoparticles/Co:Ni=50:50 (sample 9), Co-Ni/CF composite (sample 10), Co-Ni /CF/ β -CDx composite (sample 11), Co-Ni/C- powder composite (sample 12).

52°, 55°) in the case of composites (samples 6-8). Some impurity phases of NiO_2 ($2\theta=72^\circ$) and SnO_2 ($2\theta=28^\circ, 70^\circ, 76^\circ$) are present.

In Fig. 5c XRD spectra of sample 9 presenting Co-Ni nanoparticles synthesized at a ratio Co:Ni=50:50 and samples 10-12 presenting their carbon nanocomposites with a matrix respectively of CF, CF in the presence of β -CDx and C-powder are demonstrated. XRD analysis has proved the formation of two main phases: Co (fcc) ($2\theta=12^\circ, 34^\circ$) and Ni (Fcc) ($2\theta=34^\circ, 38^\circ, 44^\circ$). In the case of composites (samples 10-12) based on carbon matrix a phase of carbon ($2\theta=26^\circ, 45^\circ$) is determined, as

well as impurity phases of CoO_2 ($2\theta=20^\circ$) and NiO_2 ($2\theta=62^\circ, 72^\circ$).

The XRD analysis proves that in all cases of the synthesis of intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles and their carbon nanocomposites the formed phases are in agreement with the phase diagrams of the respective binary (Sn, Ni-Sn, Co-Ni) systems. According to the literature data for the Co-Sn particles the more suitable phase for electrode materials is CoSn_2 , and for the Ni-Sn particles - the Ni_3Sn_4 phase. In the case of Co-Ni nanoparticles the phases of Co and Ni identified them as good soft magnetic materials for biomedical applications.

4. CONCLUSION

The performed template synthesis of intermetallic nanoparticles using carbon support is a suitable approach to obtain new nanocomposites with Co-Sn, Ni-Sn, and Co-Ni nanoparticles to be used as electrode and magnetic materials. The conducted study has shown that the different supports influence the nanoparticle's morphology and specific surface area. The SEM images indicate that the morphology of the synthesized intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles and their carbon-based nanocomposites is typical for alloyed materials. The synthesized particles are different in shape and size, which is close to the carrier particle form. For the size and shape of the particles during their formation the most suitable carrier is carbon powder, because in this case the particles are characterized by a good dispersion and the aggregation is low expressed. The EDS analysis proves the presence of Co, Sn, Ni, O, C, F elements, and shows that the elemental composition reproduces the ratio between the relevant metallic components set up in the initial reaction solutions.

The intermetallic Co-Sn and Ni-Sn nanoparticles are characterized by β higher specific surface area than that of their graphite-based nanocomposites, while the graphite-based composites with Co-Ni nanoparticles have a better specific surface area compared to the nanoparticles. The supports used do not affect the phase composition of the synthesized intermetallic nanoparticles. The formed phases depend on the ratio between the metallic components and are in accordance with the relevant phase diagram of the binary Co-Sn, Ni-Sn, Co-Ni systems.

The use of a carbon support in the synthesis of intermetallic nanoparticles through the borohydride reduction is a suitable technique for *in situ* obtaining of carbon-based composite with nanoparticles. The carbon nanocomposites with intermetallic nanoparticles thus prepared will be investigated in our next work as electrode materials alternative to the graphite electrodes in Li-ion batteries and also as magnetic materials to be used in biomedicine. We expect them to be good electrode and magnetic materials on the basis of the results for the morphology, specific surface area, elemental and phase composition obtained in this study.

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