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STUDY OF CARBON-BASED NANOCOMPOSITES WITH INTERMETALLIC (Co-Sn, Ni-Sn) NANOPARTICLES

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Abstract. Intermetallic (Co-Sn, Ni-Sn) nanoparticles are synthesized through a borohydride reduction with NaBH4 in a mixture of aqueous solutions of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $SnCl_2 \cdot 2H_2O$ at different mass ratios Co:Sn and Ni:Sn. Subsequently, carbon - based nanocomposites are obtained. A "template" technique which involves borohydride reduction of intermetallic nanoparticles on a support (carbon foam, carbon powder, graphite) is used. Samples are studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis. The influence of the different supports used on the morphology, structure, phase composition and element composition of the synthesized composite materials is investigated. Phases, $CoSn_2$ (Co:Sn = 1:2), Co_3Sn_2 (Co:Sn = 3:2), Ni_3Sn_2 (Ni:Sn = 3:2), Ni_3Sn (Ni: Sn = 3:1) are achieved. They are in correspondence with the phase diagrams of the Co-Sn and Ni-Sn binary systems.

1. INTRODUCTION

A large number of studies in the area of energy storage are focused on the synthesis of new anode materials as alternatives to graphite. Such interst is caused by the need of producing a new generation lithium ion batteries (LIB) that will have better characteristics than the conventional ones. At present, all commercially used negative electrode materials for LIB are made of carbonaceous materials. They have a relatively low theoretical specific capacity (i.e. 372 mAh/g for graphite) and no further improvement can be made. This no longer meets the requirements of the intensive development of portable electronic products and electric vehicles.

Recently, researchers focus their attention on materials with a significantly higher capacity such as Sn, Si, and Sb. Sn, in particular, has drawn interest because the lithiation reaction during the charge/discharge cycle involves alloys formation of Li_xSn alloys with a maximum *x* value of 4.4. This equals to a maximum theoretical capacity value of 993 mAh/g, which is about 2.7 times higher than the theoretical one obtained with a graphite anode [1]. Despite this exceptional characteristic, pure Sn cannot be practically used due to the very high volume change during Li uptake and removal that leads to a destruction of the electrode material and poor capacity retention. To minimize such detrimental effect, two different approaches have been proposed: a creation of a multiphase electrode and a size reduction of the host material. The active material in multiphase electrodes is surrounded by an inert phase which buffers the volume change during the lithium alloying process. Binary tin-alloys (M_xSn_y) are promising materials to be used instead of pure Sn. A large number of studies have been focused on preparing Ni-Sn, Co-Sn, and Cu-Sn alloys [2-4]. Reductive precipitation with $NaBH_4$ is often used by researchers to synthesize intermetallic nanoparticles. This method represents the so called

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"bottom-up" technology which is opposite to the mechanical "top-down" grinding and alloying by ball milling. The size of the precipitated nanoparticles can be controlled by varying several parameters (i.e. precursor concentration, temperature, complexing agent, etc.) [5].

In addition, a new generation nanocomposites which combine the stability of graphitized carbon with a material showing a large capacity towards lithium are obtained[6,7]. Classic Ni or Cu supports with a coarse structure are replaced with porous fine grained electrode materials known in the literature as *foam*. These foams have micropores, which helps to increase energy and power density of the electrodes. Porous carbon - based nanocomposites which consist of carbon foam (C-foam) and metal nanoparticles can be obtained. Alternatively, carbon powder or graphite can also be used as supports in order to make carbon based/intermetallic nanoparticles nanocomposites. Their potential use is in electrochemical power sources, as well as in other areas such as biotechnology, food packaging, biology, medicine, solar cells, electric vehicles and others.

In connection to this, our goal is to obtain carbon based nanocomposite material which can potentially be used as electrodes in LIB. In our work samples are sythesized through a borohydride reduction and also a template technique with different supports (C-powder, C-foam, graphite). Physico-chemical investigations are carried out to establish the influence of the carbon matrix type on the morphology and structure of the obtained composites.

2. EXPERIMENTAL SET-UP

Intermetallic (Co-Sn, Ni-Sn) nanoparticles are synthesized as an active ingredient of nanocomposites trough a borohydride reduction with $NaBH_4$ in a mixture of aqueous solutions of the corresponding chloride salts ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $SnCl_2 \cdot 2H_2O$) at different mass ratios Co:Sn and Ni:Sn. A "template" technique with a support is used as the the reaction solutions (the precursors and the reductor) are introduced simultaneously. The experiments are carried out at room temperature and atmospheric pressure. Citric acid $(HOOCCH_2)_2C(OH)COON$ is used as a complex agent. Co-Sn and Ni-Sn nanoparticles are synthesized in-situ in the pores of a modified C-foam, and in the pores formed between the carbon grains of a C- powder and graphite, which surve as supports. Carbon-based nanocomposite materials are obtained as a result. After completion of the reduction process the samples are filtered, washed with distilled water and ethanol and dried in vacuum for 24 h at 100 °C .

Ni-Sn nanoparticles are obtained through a borohydride reduction with 1 M $NaBH_4$ in a mixture of water solutions of 0.5 M $NiCl_2 \cdot 6H_2O$ and 0.5 M $SnCl_2 \cdot 2H_2O$ at mass ratio Ni:Sn=3:1 and Ni:Sn=3:2. Co-Sn nanoparticles are also synthesized through a chemical reduction with 1 M $NaBH_4$ in a mixture of 0.5 M $CoCl_2 \cdot 6H_2O$ and 0.5 M $SnCl_2 \cdot 2H_2O$ at mass ratio Co:Sn=1:2 and Co:Sn=3:2.

The morphology, structure, elemental, and phase composition of the obtained intermetallic nanoparticles synthesized with C-based support are examined by a scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffracrion (XRD). The SEM images are made with a JEOL 6400F (Japan) SEM microscope at accelerating voltage of 7 kV and also with a JEOL JSM 5300 (Japan) SEM microscope at accelerating voltage of 20 kV. The elemental analysis is done with the JEOL 6400F (Japan) SEM microscope which has an additional appliance for Energy-dispersive X-ray spectroscopy (EDS). 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 CuK_α radiation.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical study of carbon-based composite materials with intermetallic (Ni-Sn, Co-Sn) nanoparticles. SEM/EDS and XRD results

In Figs. 1a-1d SEM images of Ni-Sn nanoparticles synthesized by reductive precipitation with $NaBH_4$ at ratio Ni:Sn=3:2 and their C-based composites are presented.

The Ni-Sn nanoparticles (Fig. 1a) are characterized by a morphology typical for alloy materials. Particles with irregular shape can be seen, and they have aggregated. The Ni-Sn nanoparticles synthesized using C-powder as a support have a different shape and size (Fig. 1b). C-particles with a spherical shape are observed. Again, the particles have irregular form and have aggregated. Flake-like particles, probably from Sn, can also be seen. The Ni-Sn nanoparticles synthesized on a graphite template have a different form (Fig. 1c). Particles have irregular shape different size and have aggregated. Tubular in form particles, which are also suppoused

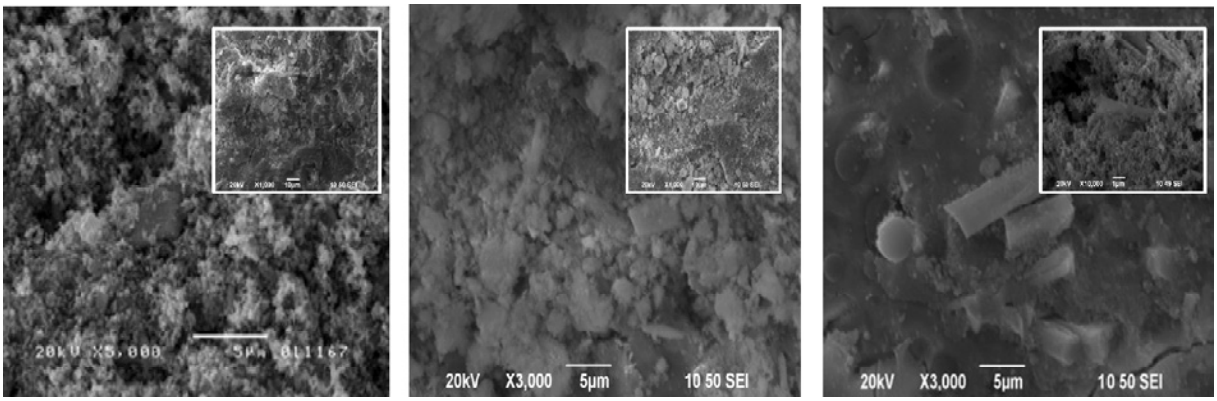

Fig. 1. SEM images at different magnification of: a- Ni-Sn nanoparticles obtained at ratio Ni:Sn=3:2, x5000, b-composite of C-powder/Ni-Sn nanoparticles, x3000, c-composite of C-F/Ni-Sn nanoparticles, x3000.

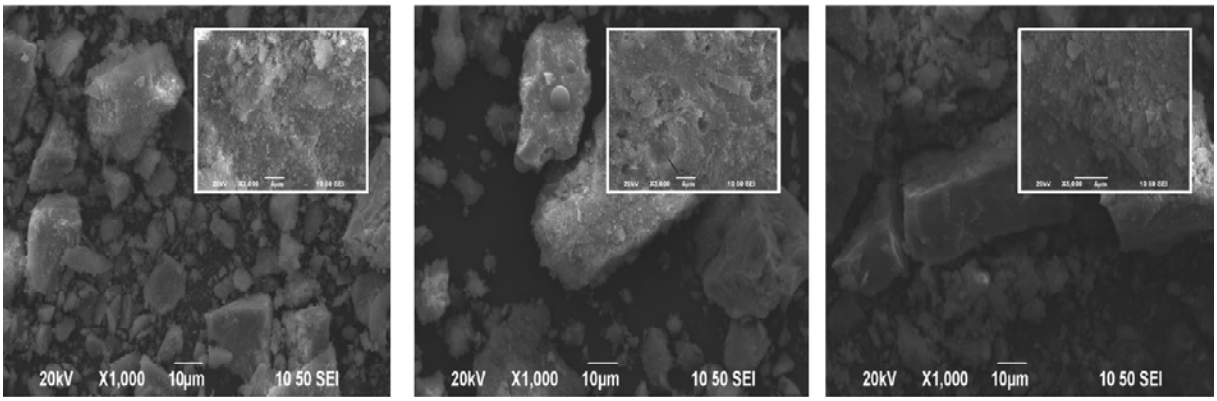

Fig. 2. SEM images, magnification x1000: a-Ni-Sn nanoparticles synthesized at ratio Ni:Sn=3:1, b-composite of C-powder/Ni-Sn nanoparticles, c-composite of C-F/Ni-Sn nanoparticles.

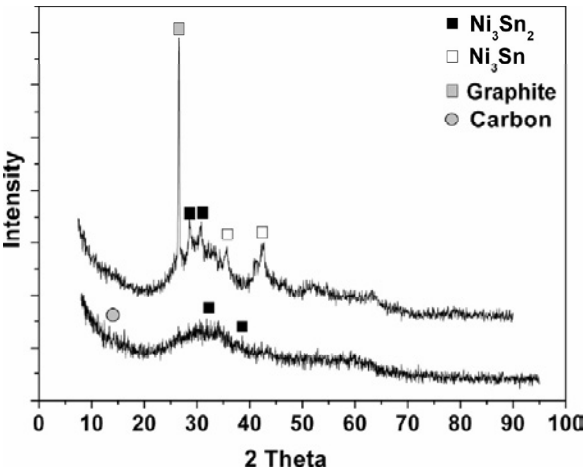

Fig. 3. XRD patterns of: a-C-powder/Ni-Sn nanoparticles (Ni:Sn=3:2), b-C-F/Ni-Sn nanoparticles.

to be Sn, are detected. It could be said that the flake structure of the graphite has an influence on the nanoparticle formation.

Fig. 2 presents SEM images of Ni-Sn nanoparticles synthesized at ratio Ni:Sn=3:1 and their composites with a C-matrix. The Ni-Sn nanoparticles synthesized with a less quantity of Sn (Ni:Sn=3:1) are characterized by a similar morphology as in the case of a ratio Ni:Sn=3:2. It is typical for the alloy materials. The nanoparticles have an irregular form and an express tendency to aggregation. The morphology of the Ni-Sn nanoparticles synthesized with C-powder as a support at a ratio Ni:Sn=3:1 is also similar to the ones where Ni:Sn=3:2. Particles irregular by shape and spherical C-grains due to C-powder template, are observed. The flake structure of the graphite used as a support has influenced the formation of the nanoparticles. Particles irregular by form and also micronized aggregated particles can be seen. When C-foam is used as a support (Ni:Sn=3:1), nanoparticles are synthesized not only in the pores of the C-foam, but also on the C-grain surface. Elemental composition of the samples according to the results of EDS analysis are listed in Table 1.

The results from the XRD analysis are presented in Figs. 3 and 4. The XRD patterns prove that one main phase of Ni_3Sn_2 is formed at a ratio Ni:Sn=3:2 in the case of the Ni-Sn nanoparticles and in the case of their composites with different C-based supports. When a graphite support is used and the ra-

Table 1. Elemental composition of the samples. Results from the EDS analysis.

Nannoparticles	Carbon matrix (90%)	Content (%) Ni	Co	Sn	C	F	Obtained ratio
Ni:Sn=3:2	-	9.90	-	6.78	-	-	3:2.03
	C-powder	3.89	-	2.52	52.27	-	3.12:2.16
	C-F	7.69	-	5.27	34.61	5.27	3.07:2.1
Ni:Sn=3:1	-	7.60	-	2.43	-	-	3.12:1
	C-powder	10.00	-	2.83	23.11	-	3.53:1
	C-F	7.60	-	2.43		36.77	3.12:1
Co:Sn = 1:2	-	-	9.25	22.63	-	-	1:2.44
	C-powder	-	6.19	18.34	11.46	-	1:2.96
	C-F	-	3.69	10.95	47.02	21.61	1:2.96
Co-Sn=3:2	-	-	10.28	7.51	-	-	3.07:2.25
	C-powder	-	14.64	8.91	43.60	-	2.92:1.78

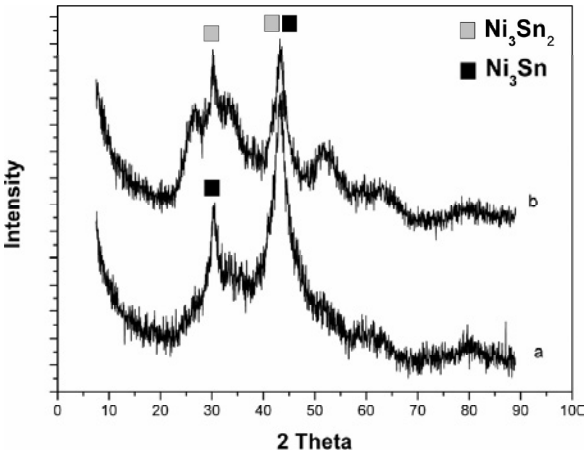

Fig. 4. XRD patterns of: a-Ni-Sn nanoparticles, Ni:Sn=3:2), b-Ni-Sn nanoparticles, Ni:Sn=3:1.

tio Ni:Sn=3:2, a phase of Ni_3Sn is also formed. When composites are prepared a phase of carbon is also established. When Ni-Sn nanoparticles are synthesized at a ratio Ni:Sn=3:1, a main phase of Ni_3Sn is obtained, which corresponds to the phase diagram of the binary Ni-Sn system a at a ratio 80% Ni – 20% Sn. It can be concluded that the different mass ratio Ni:Sn given previously at the synthesis of the intermetallic nanoparticles has a major influence on the phase formation. At the lower content of Sn (Ni:Sn=3:1) a phase of Ni_3Sn is formed, while at the higher Sn content (Ni:Sn=3:2) a phase of Ni_3Sn_2 is obtained. The formed phases are in correspondence with the phase diagram of the binary Ni-Sn system.

Figs. 5a-5c presents SEM images of Co-Ni nanoparticles obtained at a ratio Co:Sn=1:2 and their C-based composites.

The SEM results concerning the morphology of the C-based composites with Co-Sn nanoparticles (Co:Sn=3:2) show that with all the supports used (C-powder, graphite, C-foam) the nanoparticles have irregular form. They have aggregated together with C-powder and graphite grains, but are uniformly distributed.Spherical C-grains from the C-powder

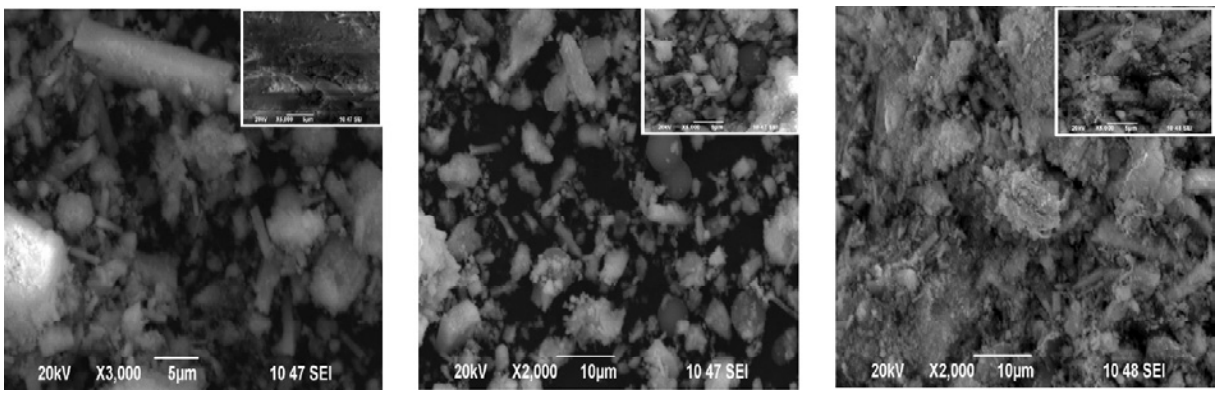

Fig. 5. SEM images at different magnification of: a-Co-Sn nanoparticles (Co:Sn=1:2), ×3000, b – C-powder/ Co-Sn nanoparticles, ×2000, c-C-F/Co-Sn nanoparticles, ×2000.

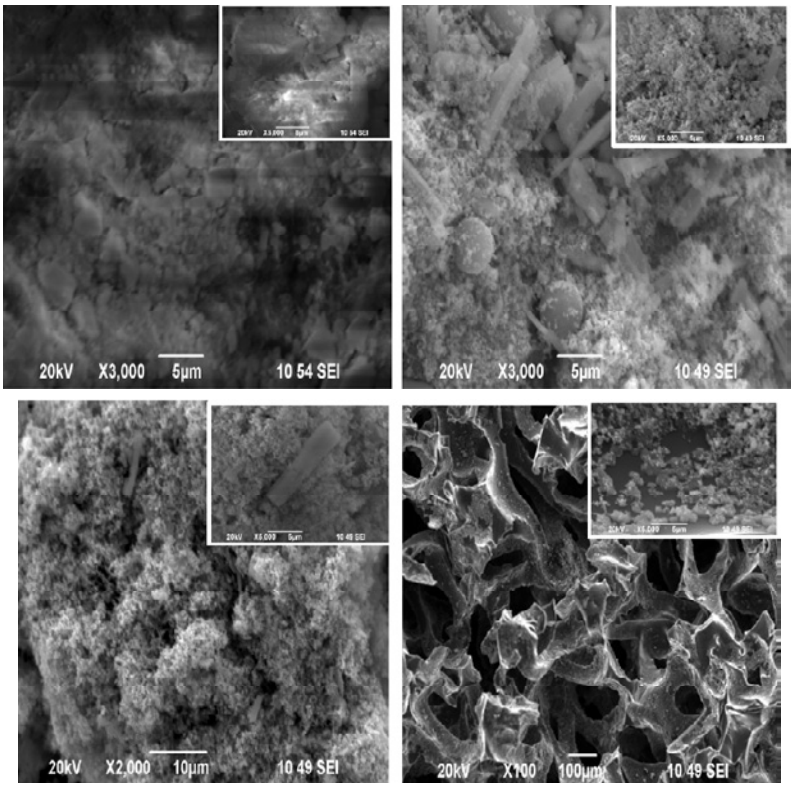

Fig. 6. SEM images at different magnification: a- Co-Sn nanoparticles obtained at a ratio of Co:Sn=3:2, ×3000, b – C-powder/Co-Sn nanoparticles, ×3000, c-C-F/Co-Sn nanoparticles, ×2000, d-C-foam/Co=Sn nanoparticles, ×100.

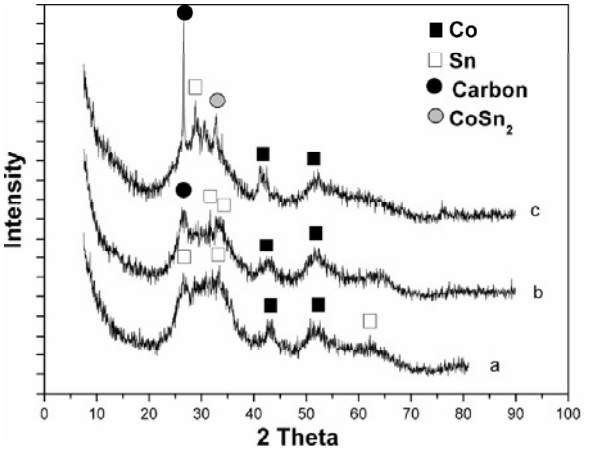

Fig. 7. XRD patterns of: a-Co-Sn nanoparticles synthesized at Co:Sn=1:2, b-C powder/Co-Sn nanoparticles, c- C-F/Co-Sn nanoparticles.

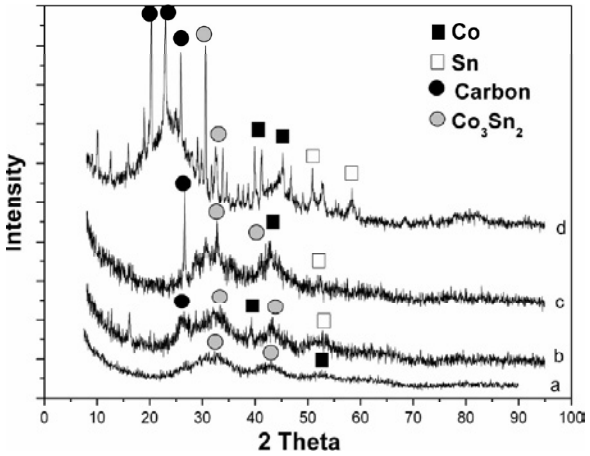

Fig. 8. XRD patterns of: a-Co-Sn nanoparticles synthesized at Co:Sn=3:2, b-C powder/Co-Sn nanoparticles, c-C-F/Co-Sn nanoparticles, d- C foam/Co-Sn.

support covered with the synthesized Co-Sn nanoparticles can also be seen. Orthogonal flake particles and particles with a form of a parallelipiped probably from Sn are formed in between. The size of the bigger particles is in the range of 200-300 μm. The morphology of the investigated samples is typical for alloy materials. It could be said that the C-based supports used, have different influence on the nanoparticle morphology, respectively on the particle dispersity.

In Fig. 6 SEM images at different magnification of Co-Sn nanoparticles synthesized at a ratio Co:Sn=3:2 and their C-based composites are presented.

Fig. 7 shows XRD patterns of Co-Sn nanoparticles synthesized at a ratio Co:Sn=1:2 and their C-based composites, while Fig. 8 presents XRD patterns of Co-Sn nanoparticles synthesized at a ratio Co:Sn=3:2 and their C-based composites

The observed peaks in Fig. 7 correspond to phases of Co, Sn and carbon. In the composite with a graphite support a phase of $CoSn_2$ is formed. The synthesis is done at a ratio Co:Sn=1:2. Fig. 8 shows that when the synthesis of Co-Sn nanoparticles is executed at a ratio Co:Sn=3:2 a main phase of Co_3Sn_2 is formed with all different kinds of supports used (C-powder, C-F, C-foam). Phases of Co, Sn, and carbon are also presented.

4.CONCLUSIONS

Reductive precipitation with $NaBH_4$ using a template technique with different supports (C-foam, C-powder, graphite) is a successful method for obtaining nanocomposites of a type inactive matrix/ nanoparticles. The reaction parameters (i.e. concentrations of both the precursors and the reductor, reaction temperature, complex agent) can be easily controlled. As a result, fine alloy powders are obtained. They can be used as anode materials instead of graphite in LIB. SEM images show that the different supports used influence the morphology and the structure of the synthesized nanocomposites. EDS analysis reveals that the preliminarily ratio of Co:Sn and Ni:Sn is kept in the obtained samples. XRD analysis proves that stable phases from the binary systems Co-Sn and Ni-Sn phase diagrams can be achieved. The morphology and phase composition of the investigated samples promise good electrochemical parameters to be used as electrode materials in LIB. Our further studies will investigate this particular direction.

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