

Ni-Sn ALLOY CARBON-CONTAINING NANOCOMPOSITES AS ALTERNATIVE ANODE MATERIALS TO THE GRAPHITE ELECTRODES IN LI-ION BATTERIES

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Abstract. Ni-Sn alloy powder is synthesized through a borohydride reduction with NaBH_4 in a mixture of aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at mass ratio Ni:Sn=45:55. The ratio is chosen in accordance with the Ni-Sn binary system phase diagram. Intermetallic Ni-Sn nanoparticles are also obtained applying a template technique which involves the use of a carbon-containing support (graphite, carbon powder, carbon foam). As a result carbon - containing nanocomposites are prepared. The samples which are Ni-Sn alloys and carbon-based nanocomposites 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 and surface elemental composition of the synthesized composite materials is investigated. The surface element composition has proven the existence of the Co and Sn. The ratio Ni: Sn=45:55 set in the intermetallic nanoparticles synthesis is approximately kept. Phases of Ni_3Sn_2 , Ni_3Sn_4 , Ni_3Sn , and NiSn_2 are achieved. They are in correspondence with the phase diagrams of the Ni-Sn binary systems. The obtained Ni_3Sn_4 phase according to literature is expected to show best properties as an electrode material. The samples are electrochemically tested by a cycling voltammetry as electrode materials in Li-ion batteries.

1. INTRODUCTION

In recent years many authors are involved in the investigations on the alternative electrode materials for a new generation of electrochemical power sources. Efforts are concentrated on the production of carbon-based composite materials which will have better characteristics than those of the conventional anodes (graphite or alloys). Metal alloys and intermetallic compounds based on Sn, Sb, and Si are synthesized because of their potential use as an alternative material of the graphite electrode in Li-ion batteries. These materials are character-

ized by a high specific capacity compared to that of the graphite [1-3]. However, in the charge-discharge cycle their volume changes due to phase transformations and it leads to stress conditions which cause cracking or destruction of the tin electrode. This negative effect could be reduced by creating a two-or multi-phase electrodes, and also by reducing the size of the base material (electrode). In bi-or multiphase electrodes the active material is usually surrounded by an inert layer that serves as a buffer, increasing the mechanical stability of the electrode.

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Cu-Sn, Co-Sn and Ni-Sn intermetallic compounds can be used as electrode materials in Li-ion batteries [4,5]. Various methods are used in order to obtain nanosized alloys with different morphology [6-8]. A relatively new approach is the preparation of composites which combine the stability of graphitized carbon with a material showing a large capacity towards lithium. Thus, a high energy matrix with stable electrochemical parameters is obtained. In the new energy storage systems an inert electrode matrix is the unifying unit (for both anode and cathode). It plays a role of a micro reaction module which simultaneously serves as a current collector, and a reservoir for electrolyte and reaction products.

Metal alloys and intermetallic compounds have been a matter of great interest as an alternative of graphite electrodes which are commonly used as electrodes in Li-ion batteries. These materials have a higher volumetric capacity than the graphite. Composite electrode materials based on Li and an active material that alloys with Li (e.g. Sn), dispensed in the volume of an inactive matrix (e.g., Cu, Co, Ni), can replace the graphite electrodes in Li-ion batteries. The inactive matrix (Cu, Co, Ni) helps reducing the mechanical stress caused by the movement of Li ions between the electrodes during the charge/discharge cycles. But these alloys are characterized by a low life cycle, which limits their use. The cyclic performance of such composites can be improved by using active particles sized at the micro- to nanodimensional scale (intermetallic nanoparticles).

The perspective features of these nanocomposites based on intermetallic nanoparticles used as electrode materials determined *the purpose of our previous investigations*. The need of finding alternative materials to graphite electrodes in Li-ion batteries generated our idea to use a C-containing support to carry out a template synthesis of intermetallic Cu-Sn, Co-Sn, Ni-Sn nanoparticles and in this way to be prepared in-situ nanocomposite materials for electrodes [9-14].

The nanoparticles with a slight dispersion exhibit unique conductive, magnetic, optic, and mechanical properties. They can be synthesized through a chemical or electrochemical reduction of a suitable metallic ion applying the so-called template synthesis that uses supports. As template supports can be used porous ceramic materials: SiO₂ and molecular sieves a type MCM-41 (SiMCM, AlMCM). In our opinion the carbon-containing matrixes such as carbon-foam, carbon-powder, graphite, and β -cyclodextrin are also of interest as a sup-

port for a template synthesis. We have used as supports carbon foam (C-foam), graphite (CF), C-powder (C-powder) in our previous work [9-14]. C-foam is characterized by a porous structure and unique properties. It could be used as a light weight support (matrix) to obtain porous nanocomposites with intermetallic nanoparticles for electrodes, because it combines a good electro-chemical behavior, good electrical conductivity, corrosion stability, environmental friendly. C-powder presents C-powder grains with a spherical shape. Graphite is characterized by flake particles irregular by form.

Accordingly, the goal of this study is to obtain C-based nanocomposite materials with intermetallic Ni-Sn nanopowders for electrodes in new generation electrochemical current sources. In connection to this the purpose of this work is to execute a template synthesis of intermetallic Ni-Sn nanopowders using supports through a borohydride reduction with NaBH₄ in a mixture of water solutions of the corresponding chloride salts at a ratio Ni:Sn=45:55 in accordance with the binary Ni-Sn system phase diagram at room temperature and thus to obtain carbon (C)-based nanocomposite materials. Secondly, to carry out physic-chemical investigations to study the morphology, structure, phase composition, and surface element content of the nanoparticles template synthesized and the prepared nanocomposite materials on their basis by electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). Thirdly, to accomplish electrochemical tests of these C-based nanocomposites with the synthesized intermetallic Ni-Sn nanoparticles as positive electrodes in Li-ion battery to evaluate the influence of the carbon matrix type on the electrochemical behavior of synthesized C-containing nanocomposite materials.

2. EXPERIMENTAL SETUP

Intermetallic (Ni-Sn) nanoparticles are synthesized through a borohydride reduction with NaBH₄ in a mixture of aqueous solutions of the corresponding chloride salts (0.2M NiCl₂·6H₂O and 0.2M SnCl₂·2H₂O) at mass ratio Ni:Sn = 45:55 in accordance with the binary Ni-Sn system phase diagram. Citric acid C₆H₈O₇ is added as a complex forming agent. Nanocomposites are also synthesized by a template technique with a support. C-foam, C-powder, and fluorinated graphite CF (commercial products) are used as supports. C-foam (commercial product) used as a support is modified through impregnation with different solutions. Firstly, the C-

foam was sensibilized with a solution of SnCl_2 and activated with a solution of PdCl_2 in order to form clusters for nucleation. Then the C-foam is treated (impregnated) with the reaction mixture. When C-powder and graphite CF are used as supports, the support quantity is 20% in relation to the synthesized nanoparticles (the mass ratio nanoparticles to support (C-powder, graphite CF) equals like 80:20). The synthesis is carried out in the so-called T-reactor at conditions of simultaneously introducing of the reaction solutions (the precursors and the reducing agent NaBH_4) and supports. The experiments are carried out at room temperature and atmospheric pressure. 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.

Techniques for physical-chemical study of the intermetallic nanoparticles and their C-based nanocomposites are used. The morphology, structure, and phase composition of the supports and the intermetallic Ni-Sn nanoparticles template synthesized were investigated by SEM, EDS, and XRD analyses. The morphology of the samples was examined by a JEOL JSM 6400F (Japan) SEM microscope at accelerating voltage of 20 kV in three regimes: a regime of secondary electrons (SEI regime), a regime of back reflected electrons (BEC regime), and a combined regime (SPI regime). The SEI images give information for the investigated sample surface, while the BEC images – for its chemical composition. The dark regions of the BEC images characterize the existence of atoms with a smaller atom number, while the light region brings information for an existence of atoms with bigger atom number. The elemental analysis (EDS) is made using the same SEM microscope with an appliance for Energy-dispersive X-ray spectroscopy. X-ray diffraction patterns of the C-based nanocomposites based on intermetallic nanoparticles were 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.

The electrochemical behavior of the synthesized alloys (stable phases of Ni_3Sn_2 , Ni_3Sn , and NiSn_2) and their C-based composites are investigated by a cycling voltammetry in a three-electrode cell using a laboratory cycle system BA502 Series Battery Analyzer. The tested nanocomposite electrodes are prepared by spreading (one-side) of the obtained C-matrix/nanoparticles composite on a Cu foil. Electrode composition is as follows - 80 % (w/o) anode materials, 10 wt.% - TAB2 (Teflonized Acetylen Black), and 10 wt.% PVDF (polyvinylidenfluoride)

binder in 1-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry. The electrodes are dried at 120 °C in a vacuum oven for 12 h and then pressed to enhance the contact between the active materials and the conductive carbons. The galvanostatic tests are carried out in a three-electrode laboratory-type metallic cell (prototype of 2032 button cell), using metallic Li foil as counter and reference electrodes. The electrolyte is 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1 in volume). The water content in the electrolyte is under 30 ppm. Test cell are assembled in a glove box under a highly pure, dry argon atmosphere. The cell was cycled at room temperature, respectively discharged and recharged at a constant current densities with 0.1-C rate between 50 and 1500 mV vs. Li/Li+. Cyclic voltammograms (CVs) are measured at a scan rate of 0.1 mV/s using a potentiostat in the same three-electrode cells. The same electrolyte, which was used for the galvanostatic test, in the range of the open circuit voltage (OCV) of the uncharged electrodes and 50 mV vs. Li/Li+ as vertex potential is used.

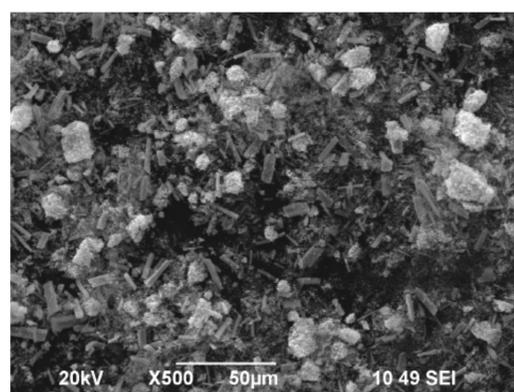
3. RESULTS AND DISCUSSION

3.1. Physical-chemical study of Ni-Sn alloy and their carbon-containing composites. SEM/EDS and XRD results

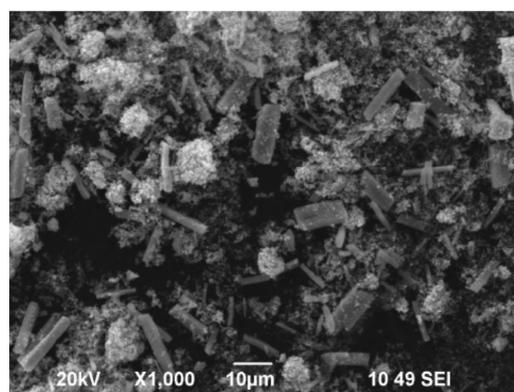
In Fig. 1a-1c SEM images of Ni-Sn nanoparticles synthesized through a borohydride reduction with NaBH_4 at a ratio Ni: Sn=45:55 are shown. The micrographs are made at different magnification. These images show Ni-Sn nanoparticles which are different in size. Small particles of 20- 30 nm are observed. However, bigger rectangular particles probably from Sn can be also seen.

Fig. 2 presents SEM images of carbon-containing composites based on Ni-Sn nanoparticles (Ni: Sn=45:55) and graphite CF as a matrix. The ratio of Ni-Sn alloy to graphite CF support is 80%: 20%. When fluorinated graphite is used as a support, the SEM images show flake like particles. This is the morphology of the graphite itself. These graphite flake like particles enclose the active intermetallic nanoparticles and prevent them from agglomeration.

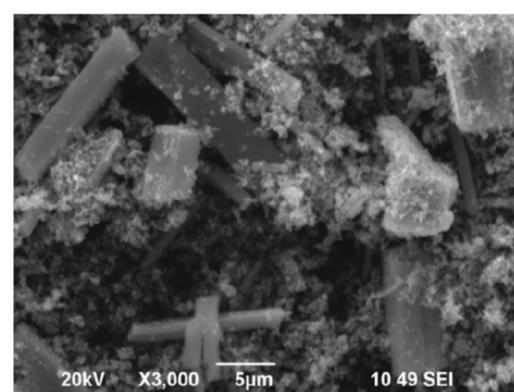
EDS spectrum for a distribution of the elements of Co and Sn on the Ni-Sn alloy (Ni: Sn=45:55)/ graphite CF matrix composite surface made in point sp¹⁷ (Fig. 2c) is given in Fig. 3. The elemental composition (in weight and atom percents) made in the



a - x500



b-x1 000



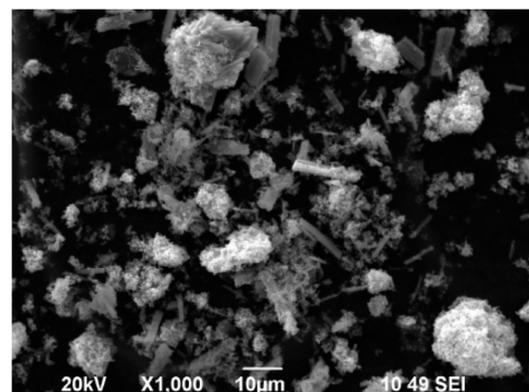
c-x3 000

Fig. 1. SEM images of Ni-Sn nanoparticles (Ni:Sn=45:55) at a different magnification: a – x500, b – x1 000, c – x3 000.

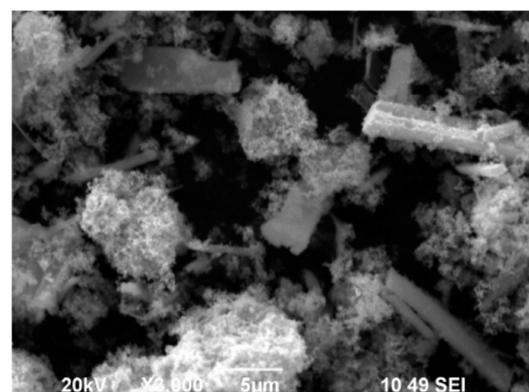
same point on the investigated sample surface are also given in Table 1.

Based on the results obtained from EDS analysis it could be said that the ratio Ni: Sn=45:55, previously given in the initial solutions, is nearly kept at the synthesized Ni-Sn nanoparticles using graphite as a support.

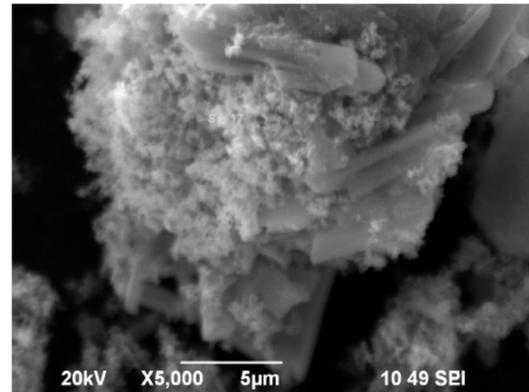
Fig. 4 is referred to SEM images of Ni-Sn alloy (Ni: Sn=45:55)/C-powder matrix composite (Ni-Sn alloy: C-powder = 80%: 20%). The Ni-Sn



a - x1 000



b - x3 000



c -x5 000

Fig. 2. SEM images of Ni-Sn alloy (Ni:Sn=45:55)/graphite CF composite at a different magnification: a - x1 000, b - x3 000, c - x5 000.

nanoparticles synthesized using C-powder as a support have a different irregular shape and size. Some of them are aggregated. The particles with a spherical shape presenting C-powder grains covered with the Ni-Sn alloy are also observe

Data from the EDS analysis of the Ni-Sn alloy (Ni:Sn=45:55)/C-powder matrix composite are given in Fig. 5. Figs. 5a and 5b show SEM images of these nanocomposites, while Fig. 5c presents the EDS spectrum of the surface element composition.

Table 1. Elemental composition of the Ni-Sn alloy/graphite composite.

Element	Intensity	Weight %	Weight %	Atomic %
C K	0.8128	15.87	0.70	43.28
O K	0.3393	16.29	0.94	33.34
Cl K	0.8674	2.00	0.13	1.85
Ni K	0.9504	11.93	0.44	6.65
Sn L	0.8814	53.91	0.84	14.88
Totals		100.00		

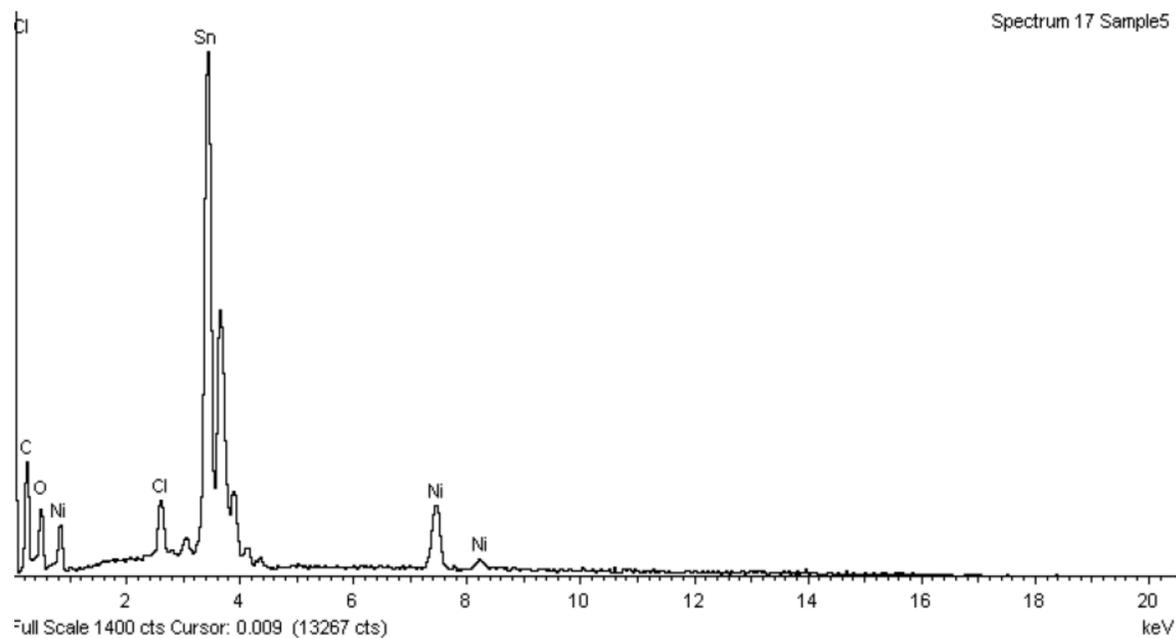
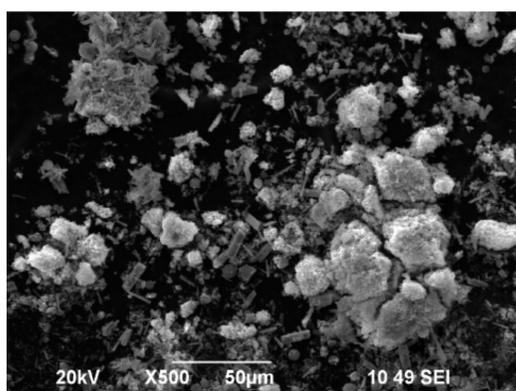
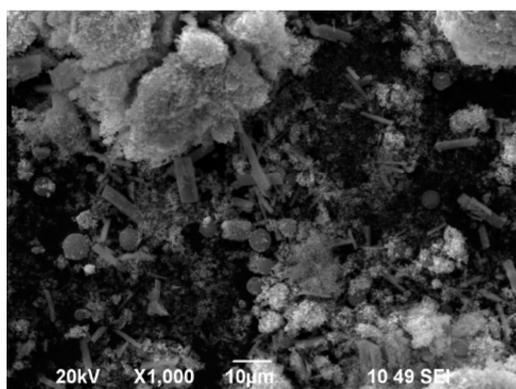


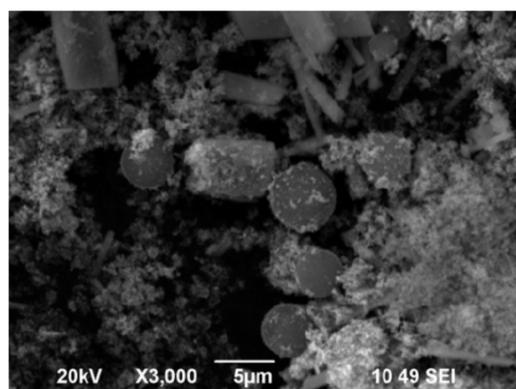
Fig. 3. EDS spectrum of Ni-Sn alloy (Ni:Sn=45:55)/graphite CF composite in a point sp¹¹, shown in a Fig. 2c.



a - x500



b - x1 000



c - x3 000

Fig. 4. SEM images of Ni-Sn alloy (Ni:Sn=45:55)/C-powder composite at a different magnification: a – x500, b – x1 000, c – x3 000.

On SEM image in Fig. 5b a point sp¹¹, where EDS analysis has been performed, is indicated, see also Table 2.

In Fig. 6 SEM images of Ni-Sn alloy/C-foam matrix composite at a different magnification are

shown. The SEM images exhibit that Ni-Sn nanoparticles are distributed in the pores of the C-foam. Aggregates between them are also observed. The small particles are in size of 20-30 nm. The bigger rectangular particles (probably from Sn) can be also seen.

Results from the EDS analysis of this sample are presented in Fig. 7 and Table 3. It could be said that the ratio Ni:Sn=45:55 set in the nanoparticle synthesis is approximately kept in the obtained nanoparticles. It can be also seen that the surface content of Ni and Sn is smaller than that one in the other cases of support used.

In Fig. 8 are compared XRD patterns of C-based nanocomposites based on different C-containing matrix and Ni-Sn nanoparticles synthesized at ratio Ni:Sn=45:55.

The XRD analysis proves the formation of Ni₃Sn₂ and Ni₃Sn phases (Sample 1), NiSn₂ and Ni₃Sn phases (Sample 2), Ni₃Sn₄ and Ni₃Sn phases (Sample 3), Ni₃Sn (Sample 4). In this particular study we aimed to obtain Ni₃Sn₄ phase as it is expected to show best properties as an electrode material in Li-ion batteries according to literature. It means that the graphite (CF) is the better matrix for the Ni-Sn alloy.

3.2. Electrochemical study - Cyclic voltammetry (CV)

Fig. 9 (a-b) presents CV curves of Ni-Sn alloy and Ni-Sn alloy/CF composite respectively. In the first cathode scan (curve 1) in the both cases of Ni-Sn alloy and Ni-Sn alloy/CF composite weak wide cathode peaks at about 1.1 V and 0.3 V can be seen. The peak at ~1.1 V may be due to partial decomposition of the electrolyte and formation of SEI film on

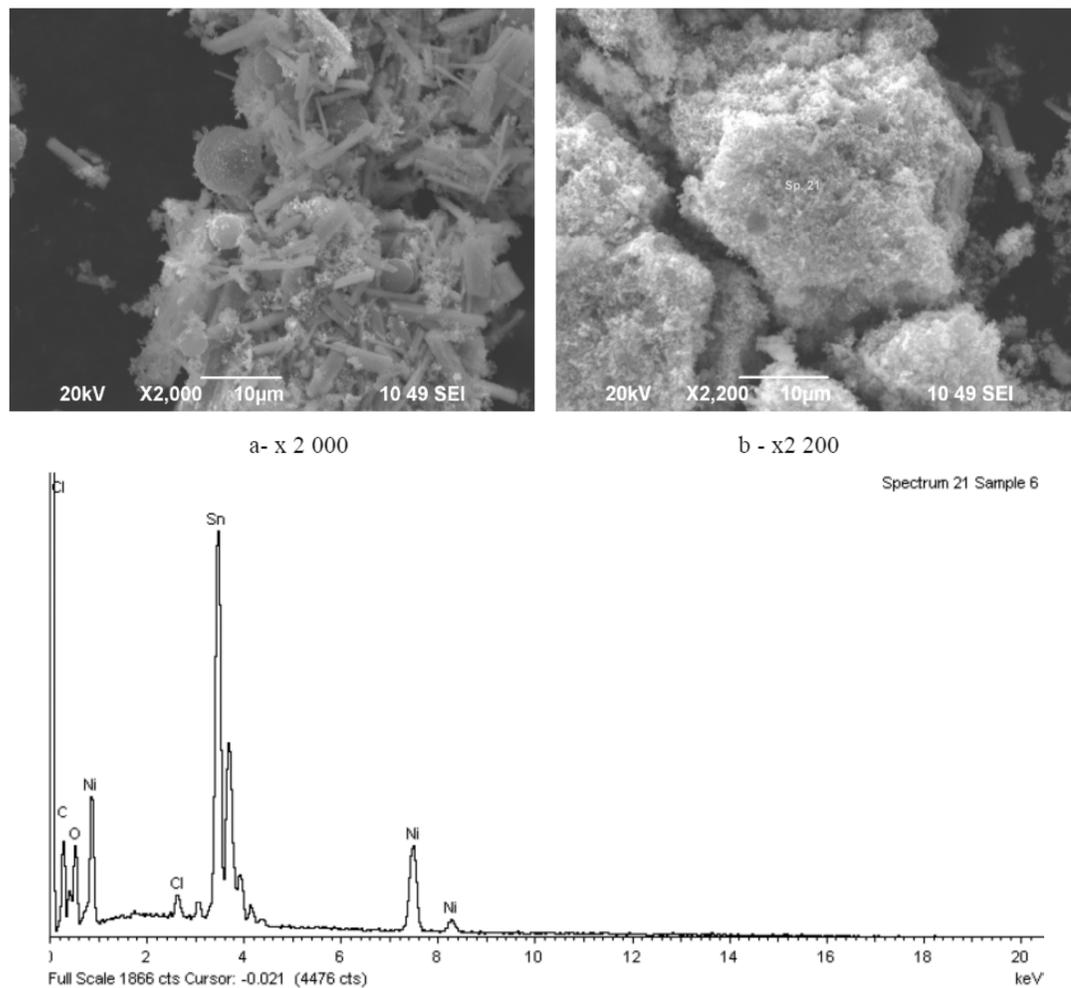


Fig. 5. SEM images and EDS spectrum of Ni-Sn alloy (Ni:Sn=45:55)/C-powder composite: a x 2 000, b – x 2 200, c – EDS spectrum in a point sp²¹, shown in a Fig. 5b.

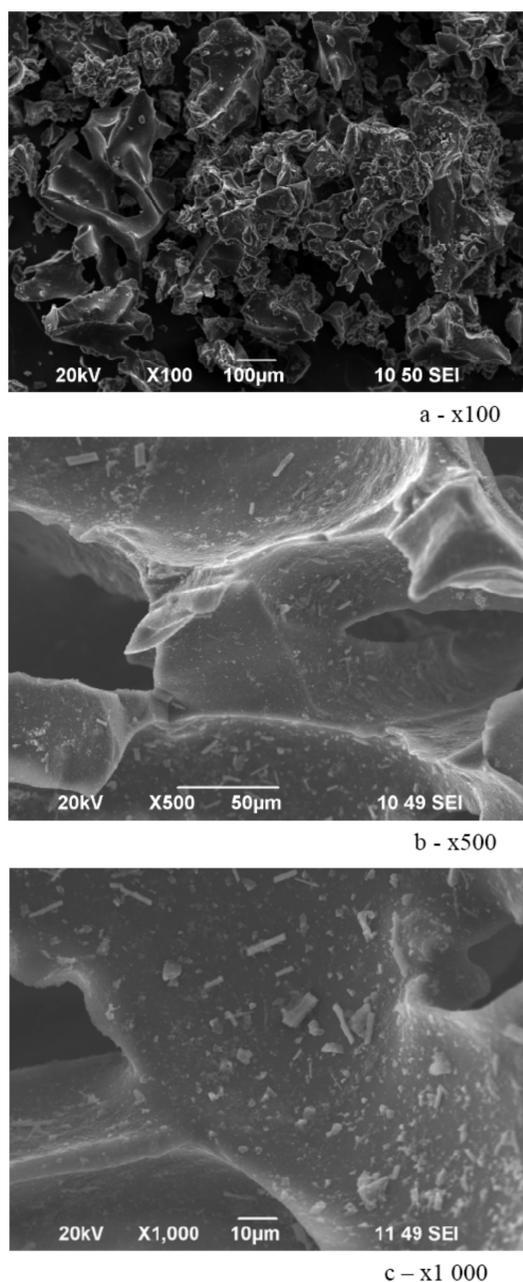


Fig. 6. SEM images of Ni-Sn alloy (Ni:Sn=45:55)/C-foam composite at a different magnification: a – x100, b – x500, c – x3 000.

the cathode surface. The indiscernible peak at 0.3 V is due to lithium insertion (intercalation) in the alloy, respectively in the composite material.

In the anode scan anode peaks at about 1.2 V and 0.6 V can be seen in both cases. These peaks are due to the lithium deintercalation (delithiation-extraction) of Sn and SnO, respectively to a partial decomposition of Li₂O.

The cathode peaks disappear and are indiscernible in the second and third cycles (curves 2 and 3) for both cases of alloy and nanocomposites. This is associated with the decomposition of the electrolyte and the formed SEI film and/or reduction of surface impurities (SnO/SnO₂).

In the CV curves of graphite, CF supported nanocomposites, there is little decrease of the currents with cycling, which implies good cyclability of nanocomposite electrodes. This means that cyclability of alloy electrodes is improved due to the graphite CF support adding. This is verified by charge/discharge cycling tests.

Cyclabilities vs. cycle number of Ni-Sn nanoparticles and Ni-Sn/CF nanocomposites are compared in Fig. 10. This Figure shows the cycle life behavior of Ni-Sn alloy and Ni-Sn alloy/CF composite electrodes using the constant current charge/discharge mode. The Ni-Sn alloy sample shows higher irreversible capacity at the 1st cycle (about 350 mAh/g). Although that the Ni-Sn alloy has a

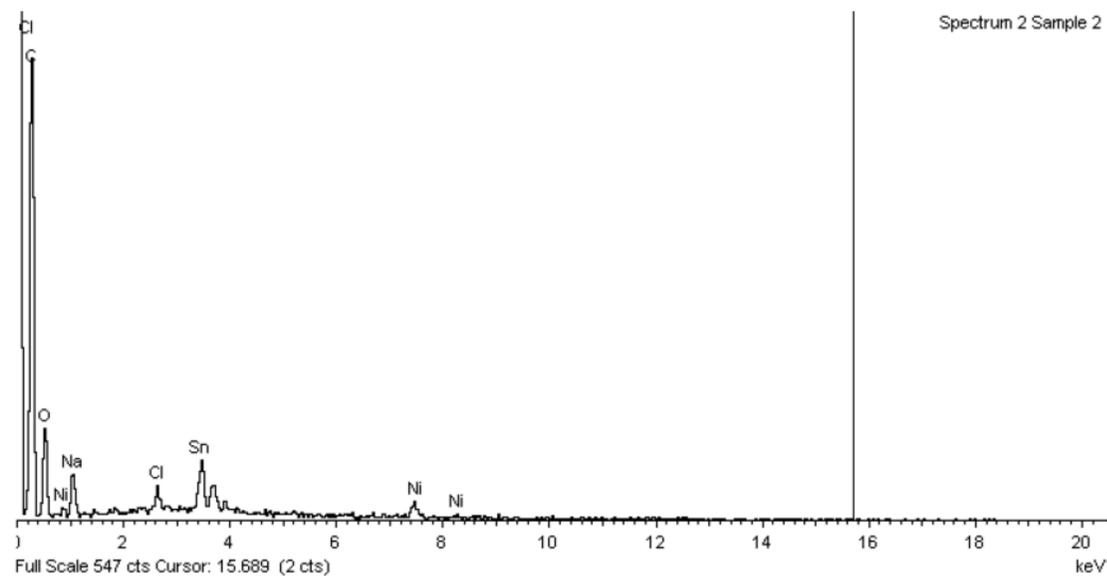


Fig. 7. EDS spectrum of Ni-Sn alloy (Ni:Sn=45:55)/C-foam composite.

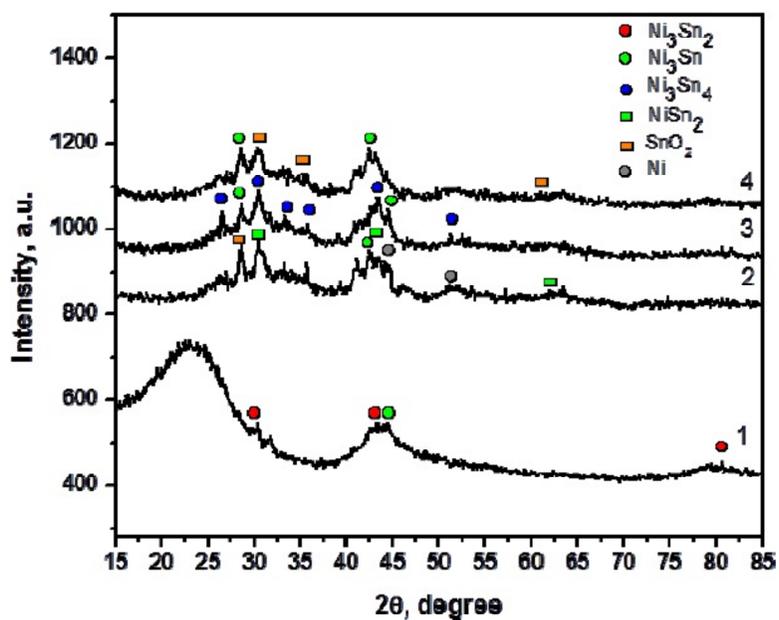


Fig. 8. XRD patterns of C-based nanocomposites with Ni-Sn nanoparticles synthesized at ratio Ni:Sn=45:55: 1-Ni-Sn alloy/C-foam, 2-Ni-Sn alloy, 3-Ni-Sn alloy/graphite CF, 4-Ni-Sn alloy/C-powder.

higher specific capacity compared with the graphite CF containing sample, in both of the samples a comparable capacity loss of 30% for 10 cycles is observed. This can be explained with the higher surface area and the presence of oxide impurities. The electrode prepared based on Ni-Sn alloy/CF nanocomposite has a better performance during cycling. The graphite CF containing sample shows higher irreversible capacity at the 1st cycle. It shows almost a stable capacity also during the first ten charge/discharge cycles. The cyclability, respectively the stability of the Ni-Sn alloy electrodes can be improved by adding C-containing support, respectively graphite support. The presence of different active areas in the composites facilitates volume expansion and prevents disintegration of the electrode and also make the cyclability better.

Table 2. Elemental composition of the Ni-Sn alloy/powder composite.

Element	Intensity	Weight %	Weight %	Atomic %
C K	0.7805	14.01	0.65	36.74
O K	0.3811	20.59	0.87	40.52
Cl K	0.8499	0.89	0.10	0.79
Ni K	0.9428	17.87	0.44	9.58
Sn L	0.8723	46.64	0.70	12.37
Totals		100.00		

Table 3. Elemental composition of the Ni-Sn alloy/graphite composite.

Element	Intensity	Weight %	Weight %	Atomic %
C K	1.1028	61.03	1.51	73.84
O K	0.3944	24.86	1.53	22.58
Na K	0.8529	2.43	0.28	1.53
Cl K	0.8343	0.88	0.17	0.36
Ni K	0.8042	2.85	0.51	0.71
Sn L	0.7888	7.94	0.58	0.97
Totals		100.00		

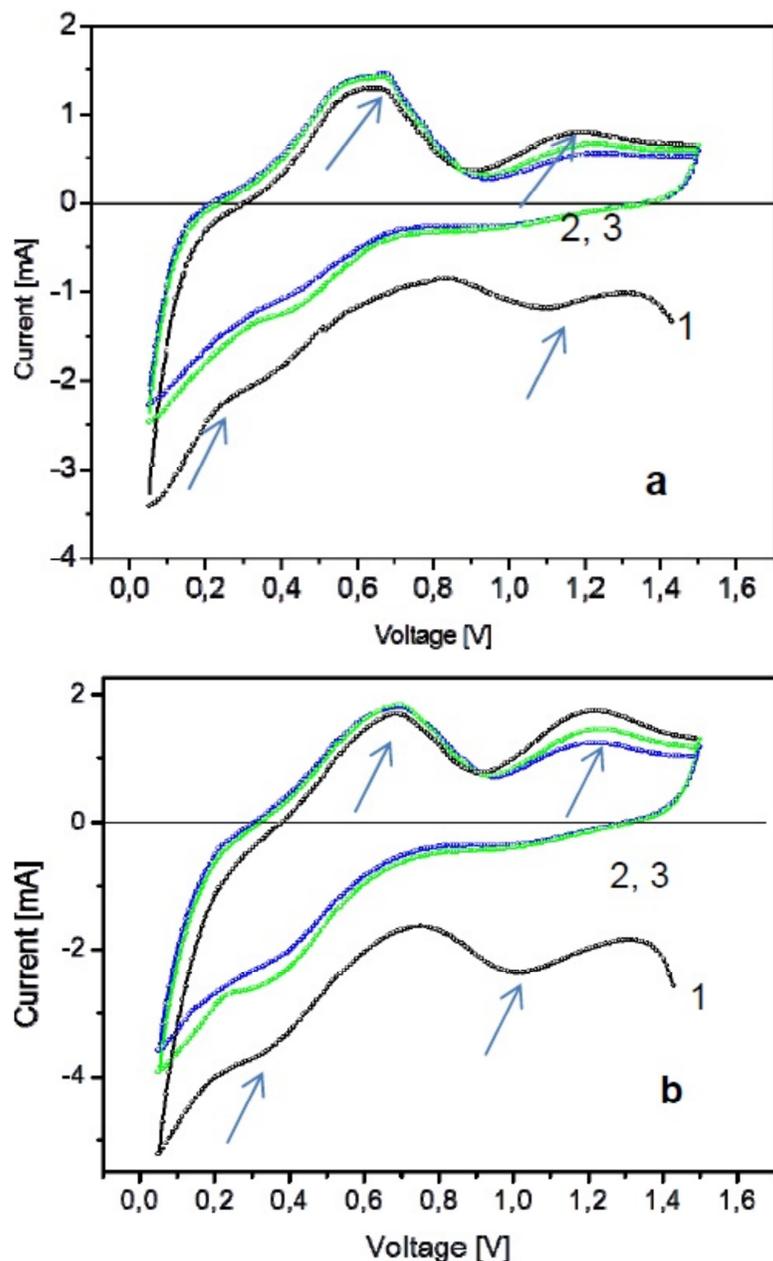


Fig. 9. CV curves of: a - Ni-Sn nanoparticles, b - composite of CF/Ni-Sn nanoparticles.

3.3. Discussion

The choice of a suitable matrix (modified C-foam, graphite, C-powder) and the optimization of the conditions for the Ni-Sn alloy synthesis could bring to essential improvement of its electrochemical behavior. It is expected that the inactive matrix (support) as a buffer surrounds the active material (Ni-Sn nanoparticles), which will lead to a decrease of the electrodes' mechanical stress due to Li insertion/removal during the charge/discharge processes, and resp. improve the cycle life. The nanosized intermetallic Ni-Sn particles used as electrodes' components contribute also to a decrease of the negative effect connected with the electrodes' destruction.

When an inactive C-based support is used, the formed stable microstructural phases of the active material prevent the electrode destruction during the cycling process and minimize the losses of a contact between the separate particles. That determines the higher irreversible capacity of the C-based matrix/Ni-Sn alloy composites.

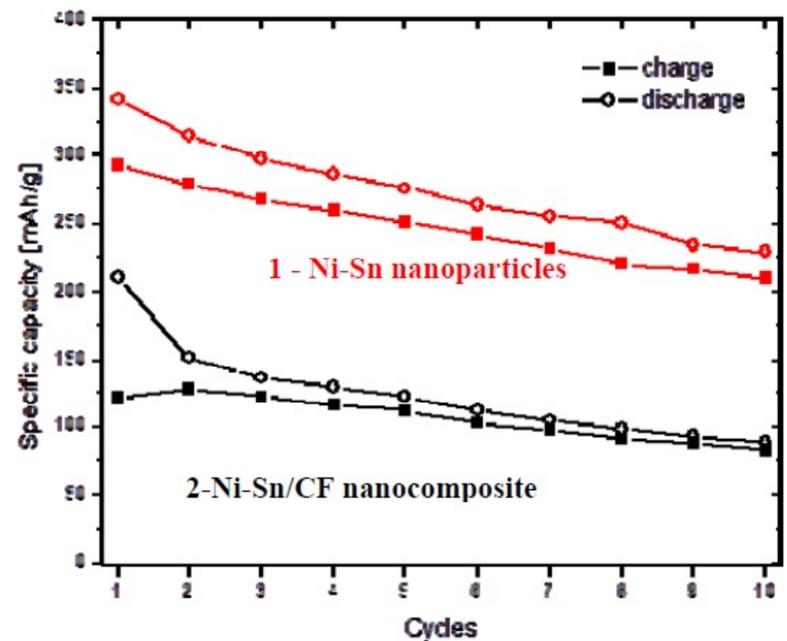


Fig. 10. Cyclability (lithium insertion/deinsertion capacities) vs. cycle number of Ni-Sn nanoparticles (1) and Ni-Sn/CF nanocomposites (2).

The better cyclability of the investigated samples is due to the presence of different active areas that facilitate volume expansion and prevents disintegration of the electrode. This is because only a part of the composite reacts at a given voltage. In this case the un lithiated phase plays the role of a buffer against the volumetric expansion of the lithiated one.

4. CONCLUSION

The performed wet brohydride reduction using a template synthesis with different C-containing supports (graphite CF, C-powder, C-foam) is an effective way and suitable down-up approach for direct in-situ obtaining of new C-based nanocomposites with active intermetallic Ni-Sn nanoparticles for electrode. Fine Ni-Sn alloy powder is obtained that can be used as anode material instead of graphite in Li-ion batteries.

All of the obtained nanocomposites have a morphology which is typical for alloyed materials. Particles are evenly distributed and are similar in size. The obtained nanoparticles of 40 to 80 nm in size have an irregular shape and tend to aggregate forming aggregates of 200-300 μm in size.

The SEM images show that the different supports used influence the morphology and the structure of the synthesized nanoparticles and their nanocomposites. The graphite CF as a carbon-containing support is suitable as regards nanoparticle dispersion.

The XRD analysis proves that stable phases (respectively Ni_3Sn_4 , Ni_3Sn_2 , Ni_3Sn , and NiSn_2 phases), which are in accordance of the Ni-Sn binary system phase diagram can be achieved. The mass ratio Ni:Sn set in the synthesis of intermetallic (Ni-

Sn) nanoparticles is determining for the phase formation.

It is expected that the combination of C-matrix and intermetallic nanoparticles would reduce the mechanical stresses due to Li insertion/ removal during the charge/discharge processes, and also improve the cycle life. When being electrochemically tested, the Ni-Sn alloy/CF graphite nanocomposite electrode shows significantly better cyclability than that one of the corresponding alloys.

It is found out that the obtained intermetallic Ni-Sn nanoparticles and their C-based composites are potential anode materials and could be used as alternative materials to the graphite electrodes in Li-ion batteries. They are expected to have improved their capacity.

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