TEMPLATE SYNTHESIS OF Cu AND Cu-Sn NANOPARTICLES USING CARBON FOAM AS A SUPPORT

Ivania MARKOVA-DENEVA, Tihomir PETROV, Ivan DENEV

University of Chemical Technology and Metallurgy, 8, Kl. Ohridski blvd., Sofia, Bulgaria,
e-mail: vania@uctm.edu

Abstract

Cu and intermetallic Cu-Sn nanoparticles have been synthesized through a borohydride reduction in water solution of corresponding chloride salts by NaBH₄ using a template technique with a carbon foam as a support at room temperature and atmospheric pressure. The Cu nanoparticles have been obtained in the carbon foam pores using 1.5 M and 2.0 M CuCl₂·2H₂O solutions, as well as the Cu-Sn nanoparticles have been prepared using CuCl₂·2H₂O and SnCl₂·2H₂O solutions with the same concentration at a mass ratio Cu:Sn=40:60. The morphology of the synthesized Cu and Cu-Sn nanoparticles using carbon foam as a support has been investigated by means of SEM analysis. The XRD analysis carried out has proved the existence of Cu, Sn and Cu₁₁Sn₃ phases. Thus prepared porous carbon foam/Cu or Cu-Sn nanoparticles nanocomposites are new electrode materials for electrochemical power sources.

Keywords: Cu nanoparticles, intermetallic Cu-Sn nanoparticles, template synthesis, carbon foam

1. INTRODUCTION

The synthesis using supports known as a template synthesis is applied for obtaining of nanosized metallic particles, wires, fibers, rods, tubes [1-7]. At this method in the pores of a support (template) a metal is deposited through a chemical or electrochemical reduction of corresponding metallic ion. Porous materials like as SiO₂, molecular sieves type MCM-41 etc. are used as supports.

In our work carbon foam (C-foam) has been used for the first time as a support to realize a template synthesis of Cu and Cu-Sn nanoparticles, because the C-foam is characterized by a porous structure [2,5,6]. The C-foam is a low material cost and light weight. It is characterized by unique properties such as high mechanical strength, high electrical conductivity, low thermal conductivity, and low thermal expansion coefficient. It can be obtained through a pyrolysis and thermal treatment of cheap precursors such as coals, different polymer materials, tar-based mesoporous pitches, olive stones, coffee precipitate, and rice waste. The C-foam applications are varied due to its unique properties. Recently the C-foam has an important application as porous battery and fuel cell electrodes. Perspective materials for electrodes in contemporary energy storage systems are porous nanocomposite materials based on a C-foam and intermetallic (Cu-Sn) nanoparticles. The unique properties of C-foam and in the first play its porous structure have initiated our idea to use a C-foam as a support for template synthesis of Cu and Cu-Sn nanoparticles through a borohydride reduction method to be obtained nanocomposite materials with porous carbon matrix and active deposited in its pores Cu and Cu-Sn nanoparticles for electrodes in electrochemical power sources.

The purpose of this work is to obtain porous C-foam/active Cu or Cu-Sn nanoparticles composite materials by template synthesis of metallic (Cu) and intermetallic (Cu-Sn) nanoparticles using C-foam as a support through a chemical reduction with NaBH₄ (borohydride reduction) in water solutions of chloride salts of Cu and Sn
(CuCl₂·2H₂O, SnCl₂·2H₂O) with different concentrations and different mass ratio Cu:Sn at room temperature and atmospheric pressure to be used as electrodes in electrochemical power storage systems.

2. EXPERIMENTAL

2.1 Template synthesis of Cu and Cu-Sn nanoparticles in the pores of a C-foam from CuCl₂·2H₂O and a mixture of CuCl₂·2H₂O and SnCl₂·2H₂O at a mass ratio Cu:Sn = 40:60

A template synthesis of Cu and Cu-Sn nanoparticle is realized using a modified commercial C-foam. In this case the nanoparticles have been deposited in the C-foam pores. The Cu-Sn nanoparticles have been prepared using a mass ratio Cu:Sn=40:60. The synthesis has been carried out in a reactor ensuring a regime of consecutively introducing of the both solution of a reducing agent (NaBH₄) and support (C-foam), applying during the synthesis a mechanical stirring by a magnetic stirrer. The support used is a commercial C-foam product, which is previously wetted with the copper solutions or a mixture of copper and tin salts. Solutions of CuCl₂·2H₂O and SnCl₂·2H₂O with different concentrations (from 0.5M to 2.0M) have been used. At first 2M CuCl₂·2H₂O and 2M SnCl₂·2H₂O solutions have been prepared. The lower concentration solutions (1.5M, 1.0M и 0.5M) have been obtained through a diluting of the 2M CuCl₂·2H₂O and 2M SnCl₂·2H₂O solutions. 4.4M NaBH₄ in 14M NaOH has been applied as a reducing agent.

2.2 Investigated techniques used

The synthesized porous nanocomposite materials based on modified commercial C-foam as a matrix and Cu and Cu-Sn nanoparticles as active components were investigated by means of electron microscopy (SEM/TEM) analyses including a specific surface area diffraction (SAED) and also by XRD analysis. SEM analysis of the synthesized nanosamples was carried out on a scanning electron microscope JEOL JSM 5300 at accelerating voltage 20 kV. X-ray diffraction patterns of carbon foam 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 CuKα radiation.

3. RESULTS AND DISCUSSION

3.1 SEM investigations of the synthesized nanosized products

Figure 1 presents SEM images of Cu nanoparticles synthesized by a template technique using C-foam as a support from 0.5M CuCl₂·2H₂O solution, while in Fig. 2 are shown SEM images of Cu nanoparticles, synthesized from 1.0M CuCl₂·2H₂O solution.

Fig. 1. SEM images of Cu nanoparticles deposited using a C-foam as a support from 0.5M CuCl₂·2H₂O at different magnifications: a - x 200, b – x 1000
In Fig. 3 are given SEM images of Cu nanoparticles synthesized in the C-foam pores from 1.5M CuCl\(_2\).2H\(_2\)O solution. Figure 4 presents SEM images of Cu-Sn nanoparticles obtained using C-foam as a support from a mixture of 1.0M CuCl\(_2\).2H\(_2\)O and 1.0M SnCl\(_2\).2H\(_2\)O solutions at a mass ratio Cu: Sn=40:60.

From the SEM micrographs, shown in Figs 1 to 3, can be seen that at the lower concentration of the initial copper solution (0.5M CuCl\(_2\).2H\(_2\)O) the synthesized in the C-foam pores Cu nanoparticles are aggregated. At the higher concentration (1.5M CuCl\(_2\).2H\(_2\)O) particles with a little dispersion and about equal size have been obtained.
In Fig. 5 are shown SEM images of Cu-Sn nanoparticles synthesized using C-foam as a support from a mixture of 2.0M CuCl$_2$.2H$_2$O and 2.0M SnCl$_2$.2H$_2$O solutions at the same mass ratio Cu:Sn=40:60.

![SEM images of Cu-Sn nanoparticles](image)

**Fig. 5.** SEM images of Cu-Sn nanoparticles deposited from a mixture of 2.0M CuCl$_2$.2H$_2$O and 2.0M SnCl$_2$.2H$_2$O using a C-foam as a support at different magnifications: a - x 100, b – x 200, c – x 1000

The SEM micrographs of the Cu-Sn nanoparticles, presented in Figs. 4 and 5, have shown that with increasing of the concentration of the initial salts the quantity of the synthesized Cu-Sn nanoparticles also increases. At the highest concentration (2M solutions) it is observed uniformly filling of the C-foam pores with particles. Cu-Sn nanoparticles are deposited not only inside the pore, but also on the surface of the grains forming the pores.

### 3.2 XRD investigations of the synthesized nanosized

Figure 6 presents XRD patterns of Cu nanoparticles, synthesized respectively from 1.5M CuCl$_2$.2H$_2$O and 2M CuCl$_2$.2H$_2$O solutions at a mass ratio Cu:Sn=40:60.

![XRD patterns of Cu nanoparticles](image)

XRD patterns prove the formation of Cu phase (2θ = 56°, 65° and 98°). It is also observed Cu(OH)$_2$ phase (2θ = 20°, 30°, 43°, 45°, 48°, 69°).

In Fig.7 are given XRD patterns of Cu-Sn nanoparticles synthesized respectively from a mixture of 1.5M CuCl$_2$.2H$_2$O and 1.5M SnCl$_2$.2H$_2$O solution and a mixture of 2M CuCl$_2$.2H$_2$O and 2M SnCl$_2$.2H$_2$O solution at a mass ratio Cu: Sn=40:60.

![XRD patterns of Cu-Sn nanoparticles](image)

Fig. 6. XRD patterns of Cu nanoparticles synthesized from 1.5M CuCl$_2$.2H$_2$O and 2.0M CuCl$_2$.2H$_2$O solutions

XRD analysis of the Cu-Sn nanoparticles obtained from the both solutions of, CuCl$_2$.2H$_2$O and SnCl$_2$.2H$_2$O (1.5M и 2.0M), proves the formation of three phases: Cu$_{10}$Sn$_3$, Cu и Sn.
4. CONCLUSION

Porous C-foam/Cu or Cu-Sn nanoparticles composites have been obtained by a template synthesis of Cu and Cu-Sn nanoparticles through a wet borohydride reduction method in water solution of the corresponding salts with NBH₄ in the pores of a modified commercial C-foam. The Cu nanoparticles synthesized from CuCl₂·2H₂O solutions with different concentrations are crystalline by structure and have a low dispersion. The Cu-Sn nanoparticles prepared from a mixture of the same solutions at a mass ratio Cu:Sn = 40:60 have been deposited in the C-foam pores and also on the surface of grains forming the pores. The XRD analysis has proved the existence of Cu, Sn and Cu₁₀Sn₃ phases, which predetermine an application of these synthesized porous composite materials for electrodes in Li-ion batteries.

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LITERATURE