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Synthesis of nanocrystalline alloys in supercritical ethanol

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1. Introduction

As alternative anode materials for the lithium-ion battery, such the nanoparticle alloys as Ni_3Sn_2 and Ni_3Sn_4, $CoSb_3$ have attracted much attention recent years [1-2]. Moreover, $CoSb_3$ was found to be an excellent thermoelectric material, and its enhanced thermoelectric properties have been observed with the decreasing of the $CoSb_3$ particle size. The usual synthesis methods include ball milling or solvethermal reactions with long reaction times in hour orders.

Supercritical ethanol, comparing with other organic solvents, is considered to be an environmental benign solvent. And it is different with supercritical water, has lower supercritical temperature and pressure, and also provides a reduction reaction atmosphere. Therefore, in our research, we synthesized the nanoparticles of Ni_3Sn_2, Ni_3Sn_4 and $CoSb_3$ in supercritical ethanol, and intensively investigated the effects of the experimental parameters on the formation of these alloy nanoparticles, and determine the synthesis optimum conditions. The reaction progress was monitored at different times and different temperatures by XRD, giving insight into the reaction pathway.

2. Experimental section

The precursor solutions were prepared by dissolving the metallic salts of $SnCl_2{\cdot}H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2$ and SbCl into the ethanol (99.5%). H_2 from the decomposition of formic acid was used as the reducing agent. The batch reactor with 5ml volume was used. In typical experiments, the reaction temperatures and reaction times were in the range of 250-450 ^oC and 5-3h.The reactor was heated in the vibrating oven at the reaction temperature. After the required reaction time elapsed, the reactor was quickly took out and put into ice-water for stopping the reaction. The product was collected by centrifugation and washed with ethanol and water repeatedly. The synthesized powders were characterized with X-ray diffraction (XRD), a transmission electron microscopy (TEM).

3. Results and Discussion

1). Synthesis of Ni_3Sn_2 and Ni_3Sn_4 nanoparticles

The experimental results showed that the ratio of $Ni^{2+}$to Sn^{2+} and the temperature decided the formation of the alloy nanoparticles. And with reaction proceeding or temperature increasing, Ni_3Sn_2 and Ni_3Sn_4 were transformed into NiSn and Ni_3Sn_2, respectively. Experimental observations suggested that nanoparticle Ni_3Sn_2 and Ni_3Sn_4 were not stable intermetallic compound so that it only existed in a narrow temperature window, which was very different from the bulk states that can stably exist in a wide temperature range [3]. Fig. 1 shows the TEM images of the nanoparticles of Ni_3Sn_2, Ni_3Sn_4 and NiSn. The single nanoparticle size was in the range of 5-10 nm.

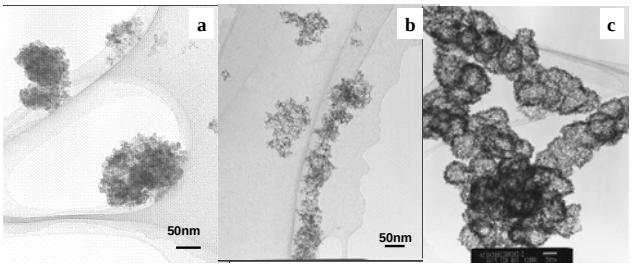

Fig. 1 The TEM images of the prepared nanoparticles of Ni_3Sn_2, Ni_3Sn_4 and NiSn. (a) Ni_3Sn-Ni:Sn=3:2; (b)Ni_3Sn_4-Ni:Sn=2:3; (c)NiSn.- Ni:Sn=1:1

2). Synthesis of $CoSb_3$ nanoparticles

The XRD analysis showed that $CoSb_3$ was the stable phase at the temperature higher than 400 ^oC, and Sb and Sb_2Co were easily synthesized at the temperatures lower than 400 ^oC. Fig. 2 shows the TEM images of the synthesized $CoSb_3$ nanoparticles. The intensive investigation on the effect of temperature and reaction time on the formation of $CoSb_3$ suggested that $CoSb_3$ be formed via the reaction of $CoSb_2$ + Sb → $CoSb_3$. But comparing with Ni_xSn_y, pure phase of $CoSb_3$ was more difficult to be synthesized, showing a trace of Sb and/or Sb_2Co was usually observed. We discussed the reasons why the pure CoSb3 can not be obtained. Our synthesis methods was highly efficient, shorting the synthesis time to 20-30min from hour order needed in the reported solvethermal methods.

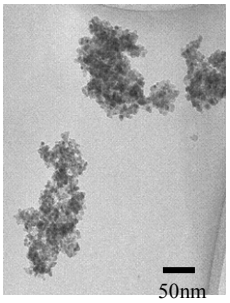

Fig. 2 The TEM images of the synthesized $CoSb_3$ at high temperature.

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[2]Xie,J..*et. al*., *J. Electrochem. Soc*., 152, 3, **2005**, A601-A606.
[3]Clemens Schmetterer *et al*., *Intermetallics*, 15 **2007**, 869-884.

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