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Nano-sized Cu₆Sn₅ alloy prepared by a co-precipitation reductive route

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1. Introduction

Recently much effort has been applied to the synthesis of uniformly sized and shape-controlled particles of metal oxide, sulfides or alloys [1-6]. Nano-sized metallic alloys have shown novel optical, catalytic, electrical and magnetic properties with respect to those of the pure metals and corresponding bulk materials. In recent years, many authors [7-9] have been working upon alternative anode materials for secondary lithium batteries. Different metals (Al, Pb and Sn) and intermetallic compounds such as Cu₆Sn₅, Sn–SnSb, Ni–Sn, SnAg and Sn₂Fe–C have been investigated as potential perspective anode materials, and some of them possess higher specific capacity than those of graphite and other carbon materials that are presently used.

However, the problems with volume changes resulting from phase transitions have not yet been solved. In 1999, Kepler et al. discovered that lithium could be intercalated into the Cu₆Sn₅ alloy, forming the system $Li_xCu_6Sn_5$ [1]. Thus, this is a material with a theoretical gravity capacity of about 350 mA h g⁻¹, and with significantly higher volume capacity, corresponding to 1656 mA h ml⁻¹, in comparison with commercial LiC_6 [1].

Many studies have been focused on lithium storage alloys since the Fuji photo film company issued a patent on tin-based amorphous composite oxides (TCO) as novel anode materials for lithium-ion batteries in 1996 [10]. Compared with the carbonaceous materials, lithium storage alloys showed a large capacity,

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ABSTRACT

Nano-sized Cu₆Sn₅ alloy powders were prepared by a co-precipitation reductive route using a hydrothermal method at 80 °C. The nano-size and morphology of the synthesized Cu₆Sn₅ alloy powders were evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The obtained morphologies, chemical compositions are comparatively discussed. A variety of synthesis parameters, such as time, capping agent and sort of reductant, has an effect on the morphology of the obtained materials, and will be particularly highlighted.

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but a low reversible capacity. It has been reported that the cycling performance of tin could be significantly improved by addition of a secondary component to form intermetallic compounds such as Sn₂Fe [11], Sn₂FeC [12], Cu₆Sn₅ [13,14] and Ni_xSn [15].

Several methods, such as high-energy ball-milling [16–19], vapor deposition [20], electro deposition [21-23] and reductive co-precipitation [24-29], have been tried to prepare nano-sized alloys with different morphologies. Baskoutas et al. have successfully prepared different nano-sized alloys such as supersaturated Ag-Cu [30], Zr₅₅Cu₁₉Ni₈Al₈Si₅Ti₅ [31], Zr-based alloys [32] and others [33] by the high-energy ball-milling method. Recently our group has synthesized a Bi₂Te₃ nano-structure with different morphologies by a hydrothermal process based on the reaction between Bi(NO₃)₃, TeCl₄, and KBH₄ in water under various conditions [34].

Among the above-mentioned methods for preparing nanosized alloys, reductive co-precipitation is shown as a simple and easy way to obtain good morphology. In continuation of the development of simple synthesized nano-sized alloys, we have investigated the influence of capping agent, stoichiometric ratio, sort of reductant and time on the morphology of nanosized alloy materials prepared by reductive co-precipitation. The Cu₆Sn₅ alloy was chosen as the material to be investigated as it has several advantages, including a strong structural relationship existing between the parent binary intermetallic electrode and its lithiated product [35-37], relatively inexpensive elements and environmental friendliness [38-40]. To the best of our knowledge, this is the first report on the synthesis of nano-sized Cu₆Sn₅ alloy via the co-precipitation method with different capping agents.



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2. Experimental

2.1. Materials and physical measurements

All the chemicals reagents used in our experiments were of analytical grade, were purchased from Merck and were used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation. Scanning electron microscopy (SEM) images were obtained on a Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscope. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV.

2.2. Synthesis of nano-sized Cu₆Sn₅ alloy

Nano-sized Cu₆Sn₅ alloy was prepared by the co-precipitation reductive method. CuCl₂ and SnCl₂ were used as the precursors in the hydrothermal synthesis. The precursors, with a Cu:Sn stoichiometric ratio of 1.2:1, were put into a Teflon-lined autoclave. The autoclave was then filled with water up to 80% of its volume. After adding sufficient KBH₄ as the reductant and pn (propylene diamine) as a complexing agent, the autoclave was sealed immediately and heated to 80 °C for the synthesis reaction. After 5 h, the autoclave was cooled down to room temperature naturally. The obtained precipitates were separated by centrifugation, washed with deionized water followed by ethanol for three times, and dried at 100 °C under vacuum for 24 h. For nano-sized Cu₆Sn₄ alloy, the experimental method was similar except a Cu:Sn stoichiometric ratio of 1.5:1 was used. The structure and morphology of the Cu₆Sn₅ and Cu₆Sn₄ powders were characterized by XRD and TEM.

3. Results and discussion

The composition of the as-prepared product was determined by XRD (Fig. 1). All peaks in the patterns correspond to the reflections of monoclinic phase Cu₆Sn₅, with cell constants a = 11.033 Å, b = 7.29 Å, c = 9.83 Å, which are in agreement with JCPDS 45–1488. The average particle size of the sample is about 37 nm, estimated through the Scherrer formula (Fig. 1a). In comparison with Cu₆Sn₅, prepared in the presence of pn as a capping agent, Cu₆Sn₅ prepared in the presence of PEG 600 and PEG 20000 as capping agents, showed an increase in the broadening of a peak at half-height, as the result of the decrease in particle size to 29 and 25 nm (Fig. 1b and c). On the other hand, with a change in the Cu:Sn stoichiometric ratio, Cu₆Sn₄ was synthesized (Fig. 2).

The morphology of the product was examined by SEM. Fig. 3a and b contains the SEM pictures of samples of nano-sized alloy. From the micrograph, it is observed that the nano-sized alloy is agglomerated. To reach an ideal morphology, we prepared nano-sized Cu₆Sn₅ alloy with various capping agents, such as PEG 600 and PEG 20000, in the presence of KBH₄ as a reductant (Fig. 3c and d). It shows that the utilization of PEG 20000 declines the agglomeration of the nano-sized alloy and the growth of the particles.

In continuation, the effect of the reductant sort on the morphology of nano-size alloy in the presence of PEG 20000 as a capping agent was investigated. Fig. 4 shows that the reducing agents do affect the morphology of the nano-sized alloy. The two other reducing agents that were applied are N_2H_4 and Zn.

The advantage of the wet preparation method is that the reduced metal cations are homogeneously dissolved in solution. Whereas the reduction with KBH_4 and N_2H_4 proceeded in a



Fig. 1. XRD pattern of Cu₆Sn₅, prepared at 80 °C for 5 h: (a) pn, (b) PEG 600 and (c) PEG 20000 as the capping agent and KBH₄ as the reductant.



Fig. 2. XRD pattern of Cu₆Sn₄, prepared at 80 °C for 5 h, pn as the capping agent and KBH₄ as the reductant.



Fig. 3. SEM picture of (a) Cu_6Sn_5 and pn as the capping agent (b) Cu_6Sn_4 and pn as the capping agent (c) Cu_6Sn_5 and PEG 600 as the capping agent (d) Cu_6Sn_5 and PEG 20000 as the capping agent, prepared at 80 °C for 5 h with KBH₄ as the reductant.

homogeneous way, the metal cation solution and the reductant solution being liquids, the reduction of the liquid metal cation solution with solid Zn powder is a heterogeneous process and as such is limited by the interface area of the Zn surface in contact with the solution. The consequences may be dramatic. The strong reductants KBH₄ and N₂H₄, in combination with stirring rapidly, created a large number of nuclei and further growth of the nuclei was limited. As a result, many small particles were obtained. The reduction in the presence of Zn proceeds only two-dimensionally, i.e., at the interface of the Zn powder with the metal cation solution. The rate of reduction is further limited by the mass transport of the metal cation solution to the Zn surface. Therefore, depletion of metal cations near the interface might occur. As a consequence of the rate and surface area limitation, crystal growth is favored over nuclei formation, with the result of larger particles [41].

The reduction with Zn generally yields materials with larger particle sizes. This may be explained by the facts that the standard reduction potential of Zn is higher than that of KBH₄ (-0.763 V versus -1.24 V) and that reduction with Zn is a heterogeneous process, with the reduction being limited to the interface between the solid Zn and the cation solution, whereas the reduction with KBH₄ takes place in homogenous solution. Hence, the reduction with Zn is expected to be milder and slower, and crystal growth

Fig. 4. SEM picture of Cu₆Sn₅ in presence of (a) N₂H₄ and (b) Zn as the reductant, prepared at 80 °C for 5 h with PEG 20000 as the capping agent.



Fig. 5. SEM picture of Cu₆Sn₅ in presence of (a) N₂H₄ and (b) Zn as the reductant prepared at 80 °C for 12 h with PEG 20000 as the capping agent.



Fig. 6. TEM picture of Cu_6Sn_5 prepared at 80 $^\circ C$ for 5 h, pn as the capping agent and KBH_4 as the reductant.

rate in comparison with nucleation is favored, so larger particles are yielded [42].

With the strong reducing power of KBH₄, gaseous by-products, such as H_2 , CuH_x and SnH_x , are formed beside the multiphase Cu_6Sn_5 phase. The related strong gas evolution adjacent to the nucleus formation site may hinder the growth of large particles and or agglomerates. Zn is a less strong reducing agent, so that in aqueous solution H_2 is only a minor by-product.

Fig. 5 reveals the time effect on the morphology of the nanosized alloy. On increasing the time from 5 to 12 h, the nano-sized alloy showed a dense agglomerate and the particle size was increased (Fig. 5a and b).

The morphology and size distribution of the products were further studied by TEM. A TEM photograph of the product is given in Fig. 6. The sizes of nano-sized alloy obtained from the TEM studies are in close agreement with the XRD diffraction patterns, which show sizes of 35–41 nm (Fig. 6). The TEM image (Fig. 6) shows the presence of dense agglomerates. The particles have an irregular shape and their distribution is not uniform (35–41 nm).

In comparison to other similar work, illustrated in Table 1, our work has various benefits, such as the Cu_6Sn_5 nano-sized alloy prepared in this work has high purity and crystallinity with only Cu_6Sn_5 being found, without any other intermetallic compounds e.g. Cu_3Sn or metal oxides. Also the particle size is smaller than most other works and for the first time, we have used different reductive agents to prepare the Cu_6Sn_5 nano-size alloy.

Table	1
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Characterization comparison of Cu₆Sn₅ nano-sized alloys from other similar works.

Particle size	Morphology	Method	Ref.
45 nm	dendrite	solution route	[43]
50–60 nm	amorphous	reverse microemulsion	[44]
30–40 nm	particle	chemical method	[45]
11–23 nm	mixture Cu ₆ Sn ₅ , Cu ₃ Sn and Cu ₂ O	reductive precipitation	[46]
	mixture	borohydride reduction	[47]
1.5–0.7 μm	spherical	spray pyrolysis	[48]

4. Conclusion

This approach to nano-sized Cu_6Sn_5 alloy is simple, convenient and effective, and holds potential for large-scale syntheses needed for commercial applications. Most important of all, this new approach can yield a high purity for Cu_6Sn_5 , without any other intermetallic compounds or metal oxides, by a simple and low cost hydrothermal method.

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