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# Influence of the preparation conditions on the morphology and electrochemical performance of nano-sized Cu–Sn alloy anodes

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#### Abstract

Nano-sized Cu–Sn alloy powders were prepared by reductive precipitation method combining with the aging treatment in constant temperature water bath at 80 °C. The microstructure, morphology and electrochemical property of synthesized Cu–Sn alloy powders were evaluated by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and galvanostatical cycling tests. The results indicated that the aged sample had uniform phase components, integrated particles, loose network-like structures and excellent electrochemical performance. When used as negative electrodes for lithium-ion batteries, the aged  $Cu_6Sn_4$  and  $Cu_6Sn_5$  samples delivered reversible capacities of about 340 and 370 mAh g<sup>-1</sup> up to 20 cycles, respectively.

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## 1. Introduction

New anode materials with high energy density and specific capacity are constantly high in demand compared with the conventional anode materials of graphite for lithium-ion batteries. In recent years, Li/metal alloys, such as Al, Sn, Sb and Si, have aroused much attention as negative electrodes for lithium-ion batteries, because they can offer an extremely large specific and volumetric capacity. However, they undergo severe phase changes during the lithiation and delithiation processes with severe volume expansion and contraction. This greatly limits the mechanical stability and cycle life of the electrode. A number of approaches have been attempted to overcome this problem, of which the most promising one is the preparation of superfine or nano-sized alloy anode materials [1-4].

Making the particle size of the electrode materials into nanometer scale can reduce the absolute volume variation and ion diffusion length during the lithiation and delithiation processes and thus, improve the cycle life and enhance the kinetics of the electrochemical process. However, nano-sized alloy anode materials also have some disadvantages, for instance,

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the electrochemical agglomeration, serious irreversible trapping of insert ions and unstable solid electrolyte interphase (SEI) film [1,2]. To overcome the above-mentioned disadvantages, several methods, such as high-energy ball-milling [5–8], vapor deposition [9], electrodeposition [10–12] and reductive precipitation [13–18], have been tried to prepare nano-sized alloy anodes with different morphologies, because the electrochemeical performance of nano-sized alloy anode materials could be altered greatly by changing their morphology [3,4].

Among the above-mentioned methods for preparing nanosized alloy anode, the reductive precipitation is shown as a simple and easy way to obtain good morphology and excellent electrochemical performance. In this paper, we investigated the influence of constant temperature water bath treatment (or aging treatment) on the morphology and electrochemical performance of alloy anode materials prepared by reductive precipitation. The Cu–Sn alloy was chosen as the investigated anode materials for its several advantages including the strong structural relationship existing between the parent binary intermetallic electrode and its lithiated product [19–21], relatively inexpensive elements and environmental friendliness. We found that the optimized morphology and homogeneous composition of the Cu–Sn alloy powders were achieved by proper aging treatment, which could be adjusted simply by changing the aging time.

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More importantly, the electrochemical performance of the sample was improved largely by proper aging treatment. Our work shows that the aging treatment is a simple and efficient method to improve the morphology and electrochemical property of the alloy anode materials prepared by reductive precipitation.

#### 2. Experimental

Nano-sized Cu–Sn alloy powders were synthesized by reductive precipitation of metal chlorides from aqueous solution with NaBH<sub>4</sub>. To produce the Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>6</sub>Sn<sub>4</sub> alloy powders, SnCl<sub>2</sub>·2H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O were mixed together with molar ratios of 1:1.2:3.2 and 1:1.5:3.5, respectively, and solved in distilled water to form a 0.1 M solution of Sn<sup>2+</sup>. The mixed aqueous solution was added drop-wise to 0.2 M alkaline NaBH<sub>4</sub> aqueous solution (pH > 12) under strong magnetic stirring at room temperature. The superfluous NaBH<sub>4</sub> solution was used to ensure a complete reduction of the metal ions. After co-precipitation, the Cu–Sn alloy powders in the aqueous solution were aged for 20 and 300 min in water bath with a constant temperature of 80 °C. Then, the solution was filtered and the product was washed thoroughly using distilled water and acetone. The black product was dried at 105 °C for 10 h under vacuum.

The crystal structure of obtained materials was detected by X-ray diffraction (D/Max-3A) with Co-K radiation. The morphology and particle size of the powders were observed by means of field-emission scanning electron microscopy (FE-SEM: JSM-6700).

Composite electrodes were prepared by pasting a slurry, which consists of 80 wt.% Cu–Sn alloy powder, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in *N*-methylpyrrolidinone (NMP), onto a copper foil substrate. The electrodes were dried in a vacuum oven at 110 °C for 12 h prior to use. Test cells were assembled in an argon-filled glove box using Celgard 2400 as the separator,  $1 \text{ mol } 1^{-1} \text{ LiPF}_6$ /ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1) as the electrolyte, and Li foil as the counter electrode. The cells were cycled on the arbin BT2000 battery tester at a constant current density of 0.2 mA cm<sup>-2</sup> between 0.02 and 1.30 V.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of  $Cu_6Sn_5$  alloy powder synthesized by reductive precipitation method. The diffraction pattern of non-aged sample consists of three phases: the major phase of  $Cu_6Sn_5$  and the impure phases of  $Cu_3Sn$  and



Fig. 1. XRD patterns of  $Cu_6Sn_5$  alloy powder prepared by reductive precipitation method: (a) aging at 80 °C for 300 min, (b) aging at 80 °C for 20 min and (c) non-aging.



Fig. 2. XRD patterns of  $Cu_6Sn_4$  alloy powder prepared by reductive precipitation method: (a) aging at 80 °C for 300 min and (b) non-aging.

a little  $Cu_2O$ , as shown in Fig. 1(c). The presence of impure phases of Cu<sub>3</sub>Sn and Cu<sub>2</sub>O in the non-aged sample indicates that it also contains a small amount of stannous impure phase simultaneously, which is not detected by XRD here. So, the distributing of Sn in non-aging sample is asymmetric. When the sample was aged at 80 °C, phase transformation happens gradually, which will decrease the production of impure phase. Fig. 1(b) shows that Cu<sub>2</sub>O phase disappears and Cu<sub>3</sub>Sn phase decreases greatly after 20 min aging. When aging time reaches 300 min at 80 °C, the impure phase of the sample is eliminated. As depicted in Fig. 1(a), pure  $Cu_6Sn_5$  phase has been achieved. The X-ray diffraction patterns of Cu<sub>6</sub>Sn<sub>4</sub> alloy powder are shown in Fig. 2, which is similar to Fig. 1. The non-aged Cu<sub>6</sub>Sn<sub>4</sub> sample has several impure phases, but the sample aged at 80 °C for 300 min only has two phases of Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn. The XRD measurement shows that the aging treatment improves the homogeneity of phase composition, which is due to the complete atom dispersion in aging treatment process. The homogenization of the component must be propitious to Li-ion transferring and structural maintenance during the lithiation and delithiation processes.

From the peak position and the half-height width of the Xray diffraction peak, the mean crystallite size can be calculated using the Scherrer equation. The results are shown in Table 1. It is observed that the mean crystallite size of  $Cu_6Sn_5$  alloy powder grow up markedly after aging at 80 °C. The particle size observed from FE-SEM images has the similar tendency which is illustrated as follows.

The FE-SEM images of nano-sized  $Cu_6Sn_5$  samples with different aging time are shown in Fig. 3(a–c). It can be seen

Table 1 The mean crystallite size of  $Cu_6Sn_5$  alloy powder

Sample	Mean crystallite size (nm)
Cu <sub>6</sub> Sn <sub>5</sub> (non-aging)	11.0
Cu <sub>6</sub> Sn <sub>5</sub> (aging at 80 °C for 20 min)	14.5
Cu <sub>6</sub> Sn <sub>5</sub> (aging at 80 °C for 300 min)	22.3







Fig. 3. FE-SEM images of  $Cu_6Sn_5$  alloy powder prepared by reductive precipitation method: (a) non-aging, (b) aging at 80 °C for 20 min and (c) aging at 80 °C for 300 min.

that the morphology of three samples have dramatic differences. As shown in Fig. 3(a), the primary particles of non-aged Cu<sub>6</sub>Sn<sub>5</sub> sample are too small to be identified and aggregate to large aggregations randomly. It can be contributed to that the strong reductant NaBH4 in combination with an intense stirring during the reductive process creates a large number of nuclei, which limited the growth of grains. The small particles with high surface energy tend to aggregate spontaneously to decreasing their system energy. When the non-aged sample is aged at 80 °C for 20 min, some smaller primary particles dissolve and bigger ones grow gradually. But the smaller primary particles cannot dissolve completely in this period. The residual smaller particles aggregate on the surface of bigger ones to form large secondary particles which also have slight aggregation, as shown in Fig. 3(b). When aging at 80 °C for 300 min, the primary particles and the aggregation of particles disappear completely. A loose network-like structure appears instead, which can be seen clearly in Fig. 3(c). The network formed between the particles is similar to the sinter-neck formed in the powder metallurgy (PM) incompact sintering process. The loose density of the sample aged at 80 °C for 300 min is far less than that of the non-aged one because of the loose network-like structure. The size of the particles with network-like structure is about 50 nm and has good uniformity.

Fig. 4 shows that the discharge capacities of the aged sample are markedly higher than that of the non-aged one except the first cycle. The aged  $Cu_6Sn_4$  and  $Cu_6Sn_5$  samples delivered reversible capacities of about 340 and 370 mAh g<sup>-1</sup> up to 20 cycles, respectively. The high reversible capacities of the aged sample are contributed to the low first cycle irreversible capacities and good cycling performance, as shown in Figs. 5 and 6.

Fig. 5 shows the typical voltage versus specific capacity curves of  $Cu_6Sn_5$  samples for the first cycle. Although the exact reaction mechanism of  $Cu_6Sn_5$  with Li is still not clearly understand, it is generally accepted that discharge voltage above 0.7 V is attributed to irreversible reaction of oxide impurity reduction, electrolyte decomposition and solid electrolyte interphase (SEI) film formation, discharge voltage above 0.2 V is attributed to lithium ions insert in  $Cu_6Sn_5$  to form  $Li_2CuSn$ , while discharge



Fig. 4. Cycling performance of Cu<sub>6</sub>Sn<sub>4</sub> and Cu<sub>6</sub>Sn<sub>5</sub> electrodes.



Fig. 5. Initial voltage profiles of Cu<sub>6</sub>Sn<sub>5</sub> electrodes.

voltage between 0.0 and 0.2 V corresponds to the formation of the fully lithiated Sn phase (i.e.,  $Li_{4.4}Sn$ ). In charge curve, the charge plateaus at about 0.5 and 0.8 V correspond to the reversibly formation of the  $Li_2CuSn$  and  $Cu_6Sn_5$ , respectively.

From Fig. 5 we can see that the voltage trends of two samples are similar. However, the non-aged sample shows more discharge capacities and less charge capacities than that of the aged one, which indicates that the non-aged sample has more first cycle irreversible capacities. It should be noted that the more discharge capacities of the non-aged sample mainly appear above 0.7 V in the discharge curve, which is attributed to the more irreversible reaction because smaller particle and larger surface area exists in the non-aged sample. In charge curve of the non-aged sample, the absence of the obvious charge plateau around 0.8 V, which caused by more irreversible trapping of Lions, results in less charge capacities.

Fig. 6 shows that the non-aged samples of  $Cu_6Sn_4$  and  $Cu_6Sn_5$  have relatively low Coulomb efficiency at the initial several cycles. There are following possible factors resulting in this phenomenon. In the perspective of thermodynamics, the surface



Fig. 6. Coulomb efficiency of Cu<sub>6</sub>Sn<sub>4</sub> and Cu<sub>6</sub>Sn<sub>5</sub> electrodes.

energy of nano-sized particle is very high and the system tends to reduce its free energy by decreasing the surface energy as much as possible. Therefore, almost all primary particles in the non-aged sample aggregate spontaneously to decreasing the surface energy. So the contact between the primary particles is very close but instability. In lithiation process, the aggregated primary particles can be bonded directly to form larger electrochemical agglomerations when Li-ions are extracted electrochemically. When larger agglomerated particles formed, it cannot be separated in subsequent lithiation process. The agglomeration of the particles will destroy the stability of SEI film. Some SEI films are embedded within the agglomerations and thus deteriorate the electrical conductivity of the alloy particle. Furthermore, the intrinsic and extrinsic defects with high density and high energy exist in the non-aged sample, which also results in low Coulomb efficiency at the initial several cycles by inducing more irreversible trappings of insert Li-ions [1,2].

On the contrary, the cycling performance is remarkably improved at initial several cycles by aging at 80 °C for 300 min. The following three aspects can explain this phenomenon. Firstly, the aging treatment promotes the growth of the particles and reduces the surface area, which results in the decreasing of the first cycle irreversible reaction of oxide impurity reduction, electrolyte decomposition and SEI film formation. Secondly, the high integrity and uniformity of the particles of the aged sample can largely reduce the intrinsic and extrinsic defects. Thus, the irreversible trappings of insert Li-ions become weaken. Finally, particle aggregation disappears completely and a loose network-like structure forms after aging, which greatly reduces the possibility of electrochemical agglomeration when Li-ions are electrochemically extracted from the host lattice and improves the stability of SEI film.

Fig. 6 also shows that the aged and the non-aged samples exhibit good cycling performance at the subsequent cycles following the initial several ones. The existing of inactive matrix Cu buffers the larger volume change in the course of alloying process. Accordingly, the Cu–Sn alloy anodes provide a much more stable cycling performance than pure tin metal. Nanoscale of the samples induces small absolute volume variation and short Li-ion diffusion length during the lithiation and delithiation processes, which must be propitious to improve the cycling performance. Moreover, more  $Li_2O$  in non-aged sample and uniform phase components in aged sample can, respectively, improve their cycling performance, too.

#### 4. Conclusions

In this work we have extended the investigation of Cu–Sn alloy anode by reductive precipitation method. It is proved that the aging treatment is a simple and efficient method to improve the morphology and electrochemical property of Cu–Sn alloy anode materials prepared by reductive precipitation. XRD patterns and FE-SEM images show that the samples aging at 80 °C for 300 min has uniform phase components, integrated particles and loose network-like structures. The aged sample exhibits excellent electrochemical performance, such as low first cycle irreversible capacities, high reversible capacities and good

cycling performance. When cycled at a constant current density of  $0.2 \text{ mA cm}^{-2}$  between 0.02 and 1.30 V, the aged Cu<sub>6</sub>Sn<sub>4</sub> and Cu<sub>6</sub>Sn<sub>5</sub> samples deliver reversible capacities of about 340 and 370 mAh g<sup>-1</sup> up to 20 cycles, respectively.

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