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Letter

Lithium storage properties of nanocrystalline eta-Cu₆Sn₅ alloys prepared by ball-milling

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Abstract

Nanocrystalline eta- Cu_6Sn_5 alloy powders were prepared by high energy ball-milling. Lithium ions can be electrochemically inserted into Cu_6Sn_5 electrodes, alloying with Sn to form Li_xSn alloys. Simultaneously, an inactive Cu matrix is produced, which could buffer the volume expansion of the active Sn due to the formation of Li_xSn alloys. It appears that lithium can react reversibly with the nanocrystalline Cu_6Sn_5 alloy to some extent. A reversible capacity of ~400 mAh/g has been achieved in preliminary tests. The results of ex-situ X-ray diffraction support the above proposal. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cu-Sn alloys; Ball-milling; Nanocrystalline alloy; Li-cell electrode; Electrochemical capacity

1. Introduction

The tin based glass and intermetallic alloys recently have attracted a worldwide attention as lithium storage materials because of their high volumetric capacity. The tin based amorphous composite oxide (TCO) demonstrated a high reversible capacity of 650 mAh/g. However, a 37% irreversible capacity in the initial cycle due to the formation of Li₂O, prevented it from further commercial application [1-4]. Theoretically, the intermetallic alloys seem not to have this problem because there is no oxygen in the alloy structure. The mechanism for reversible lithium insertion and extraction in MSn alloys relies on lithium alloying with Sn to form Li_xSn alloy. The nanosize inactive M matrix is generated simultaneously, which buffers the volume expansion of the active phase Sn due to its alloying with Li. Nanosize or amorphous alloy powders are usually required to realize the above process. Several alloys such as SnSb, Sn₂Fe and SnFe₃C have been investigated and the process of lithium alloying with Sn has been confirmed by in-situ X-ray diffraction [5-9]. However, a different mechanism for lithium insertion into the crystalline eta-Cu₆Sn₅ alloy has been demonstrated to be a two phase reaction to yield $Li_x Cu_6 Sn_5$ (x=13), corresponding to a theoretical capacity of 358 mAh/g [10]. We think that lithium alloying with Sn in eta-Cu₆Sn₅ could be achieved by preparing nanosize eta-Cu₆Sn₅ powders, in which 1 mole of Cu₆Sn₅ could combine with 22 moles of Li to form $Li_{22}Sn_5$ and generate 6 moles of Cu. The theoretical capacity for this process is 608 mAh/g, which is almost twice that of the mechanism to form $Li_{13}Cu_6Sn_5$ alloy.

This paper describes the synthesis of nanocrystalline eta- Cu_6Sn_5 alloy powders. Their electrochemical performance as electrodes in lithium cells was characterized. The mechanism for lithium insertion in Cu_6Sn_5 alloy was studied by ex-situ X-ray diffraction.

2. Experimental

Nanocrystalline $\text{eta-Cu}_6\text{Sn}_5$ alloy powders were prepared by high energy ball-milling. The elemental powders of Cu and Sn as well as hardened steel balls were put into the steel vial. The vial was initially evacuated and then filled with argon. The ball-milling was carried out in a Pulverisette-5 ball-milling machine (LABTECHNICS, Australia). For comparison, crystalline eta-Cu₆Sn₅ alloy was also synthesized by sintering a pellet of a stoichiometric mixture of Cu and Sn powders in argon at 400°C for 15 h. The sintered pellet was ground and sieved through a 325-mesh stainless steel sieve. The alloy pow-

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ders were characterized by X-ray diffraction on a Philips PW 1730 diffractometer with a Cu-K α radiation.

The Cu₆Sn₅ electrodes were prepared by dispersing 97 wt% Cu₆Sn₅ powders and 3 wt% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate to form a slurry, which was spread on to the copper foil. No carbon additives were added because Cu₆Sn₅ alloy has good electrical conductivity and also in order to eliminate the ambiguity caused by the insertion of lithium into carbon. The typical Cu₆Sn₅ electrode contains about 1 mg active materials and 80 μ m in thickness. Li/Cu₆Sn₅ coin cells (CR2032) were assembled. The electrolyte was 1 M LiPF₆ in EC (ethylene carbonate) and DMC (dimethyl carbonate) (Battery grade, MERCK KGaA, Germany). The cells were charged and discharged at a constant current density of 0.20 mAh/cm².

After cycling, the cells were dismantled in an argon filled glove-box (Unilab, Mbraun, USA) and the Cu_6Sn_5 electrodes were taken out. The Cu_6Sn_5 electrodes were covered by a plastic film for ex-situ X-ray diffraction.

3. Results and discussion

The eta- Cu_6Sn_5 alloy has a hexagonal structure with a space group of $P6_3/mmc$. It can be synthesized by either sintering the mixture of Cu and Sn powders or ball milling Cu and Sn powders. Fig. 1 shows X-ray diffraction patterns of Cu_6Sn_5 alloys. The sintering process produced a typical crystal Cu_6Sn_5 alloy with a small amount of impurity phase of the unreacted Sn, while the ball-milling generated fine Cu_6Sn_5 alloy powders. As the ball-milling time was increased, the diffraction peaks became broadened, indicating a decrease of the particle size. When ball-milled for 110 h, very broad diffraction peaks were observed, from which the grain size was calculated to be



Fig. 1. X-ray diffraction patterns of eta-Cu₆Sn₅ alloys. (a) Cu₆Sn₅ alloy prepared by sintered process. (b) Cu₆Sn₅ alloy prepared by ball-milling for 18 h. (c) Cu₆Sn₅ alloy prepared by ball-milling for 46 h. (d) Cu₆Sn₅ alloy prepared by ball-milling for 110 h. * α -Sn, \bigvee Cu₂O or SnO₂.

5–10 nm, using the Scherrer formula: $d = K\lambda / \beta \operatorname{Cos} \theta$ [11]. However, a small amount of tin or copper oxides were formed during the long term ball-milling, probably due to the very active nature of the nanosize Cu₆Sn₅ alloy and traces of oxygen present in the ball-milling vial.

The Li/Cu₆Sn₅ cells were cycled between 0 and 1.5 V at a constant current density of 0.20 mA/cm^2 . The lithium insertion into and extraction from Cu₆Sn₅ alloy are defined as discharge and charge respectively. The first discharge and charge profiles of Cu₆Sn₅ alloy electrodes are shown in Fig. 2. The ball-milled nanosize Cu₆Sn₅ electrode demonstrated markedly different behaviour for lithium insertion compared to that of the sintered crystalline Cu₆Sn₅ alloy. In the first discharge, nanosize Cu₆Sn₅ alloy electrode delivered a capacity of 688 mAh/g, corresponding to approximately 25 moles of lithium insertion per mole of Cu₆Sn₅ alloy. Provided lithium alloys with Sn, the maximum lithium insertion achievable theoretically is that each mole of Cu₆Sn₅ alloy can combine with 22 moles of Li to form Li44 Sn alloy, with a capacity of 608 mAh/g. As shown in Fig. 1, a small amount of Sn and Cu oxides are generated during the long term ball-milling. The extra lithium insertion capacity of 80 mAh/g observed might be caused by lithium reacting with Sn or Cu oxides to form Li₂O. And this part of lithium cannot be extracted again, which is similar to the behaviour of tin based glass. A reversible capacity of 412 mAh/g was achieved in the first charging which is 60% of the initial discharge capacity. However, the first discharge capacity for sintered Cu₆Sn₅ alloy was only 284 mAh/g. The theoretical capacity for lithium insertion into Cu₆Sn₅ to form $Li_{13}Cu_6Sn_5$ (isostructural with Li_2CuSn) is 358 mAh/g. Here, we did not achieve the theoretical capacity, possibly due to the relatively large particle size. With the scrutiny of the differential capacity vs. voltage profiles (the insets in Fig. 2), it might be seen that the ball-milled nanosize Cu₆Sn₅ electrode shows several reduction peaks, corresponding to the formation of Li₂O and various Li_xSn alloys, which is similar to the behaviours of Sn, SnO, SnO₂ and SiSnO₃ electrodes [12]. By contrast, the crystalline Cu₆Sn₅ alloy electrode only shows one sharp reduction peak, which corresponds to the topotactic insertion of lithium into Cu_6Sn_5 alloy structure to form $Li_rCu_6Sn_5$. This is in agreement with the report from K.D. Kepler et al. [10]. Consequently, the two different mechanisms for lithium reaction with ball-milled nanosize and sintered crystalline Cu₆Sn₅ alloys are proposed, as follows:

$$22\text{Li} + \text{Cu}_{6}\text{Sn}_{5} \text{ (nanosize)} \rightleftharpoons 5\text{Li}_{4,4}\text{Sn} +$$
6Cu (Alloying process) (1)

13Li +

 Cu_6Sn_5 (crystalline) $\rightleftharpoons Li_{13}Cu_6Sn_5$ (Topotactic insertion process) (2)



Fig. 2. The first discharge/charge profiles of Li/Cu_6Sn_5 cells. The insets are the corresponding differential capacity vs. voltage. (a) Ball-milled Cu_6Sn_5 alloy electrode (ball-milling for 110 h). (b) Sintered crystalline Cu_6Sn_5 alloy electrode.



Fig. 3. The ex-situ X-ray diffraction patterns of Cu_6Sn_5 alloy electrodes in the fully discharged state. (a) Ball-milled nanosize Cu_6Sn_5 alloys (ball-milling for 110 h). (b) Sintered crystalline Cu_6Sn_5 alloys.

In order to confirm these mechanisms, ex-situ X-ray diffraction was performed on the Cu₆Sn₅ electrode in the fully discharged state. The ex-situ XRD patterns are shown in Fig. 3. For the ball-milled nanosize Cu₆Sn₅ electrode in the heavily lithiated state, Li_{4.4}Sn is identified by the two diffraction peaks at $2\theta = 23.5^{\circ}$ and 39.9° . The broad $2\theta =$ 39.9° peak suggests a very fine particle size of Li_{44} Sn. However, Li₂CuSn phase was detected for sintered crystalline Cu₆Sn₅ in the fully discharged state, characterized by the diffraction peaks at $2\theta = 24.2^{\circ}$ and 40.7° respectively. The unreacted Cu₆Sn₅ phase was also presented in the XRD pattern. These unreacted Cu₆Sn₅ alloys could be responsible for the low discharge capacity of crystalline Cu_6Sn_5 alloy electrode due to the large particle size and limited kinetics for lithium insertion. No any Li-Sn alloy phase was found, which confirmed the process of lithium



Fig. 4. Discharge capacity vs. cycle number for Li/Cu₆Sn₅ cells.

insertion into crystalline Cu_6Sn_5 to form the compound $Li_rCu_6Sn_5$.

Fig. 4 shows the discharge capacity vs. cycle number for the two different kinds of Cu_6Sn_5 alloys. The capacity for both nanosize and normal crystal size Cu_6Sn_5 alloys declines on cycling quite quickly. Further work needs to be done to identify the mechanism for this phenomenon and to improve the cyclability of Cu_6Sn_5 alloy electrodes.

4. Conclusions

It was found that there were two different mechanisms for lithium reacting with ball-milled nanosize and sintered crystalline eta- Cu_6Sn_5 alloys. The reaction of lithium with nanosize Cu_6Sn_5 is an alloying process, in which lithium alloys with Sn to form Li_xSn and generates Cu simultaneously. By contrast, an insertion process takes place in the crystalline Cu_6Sn_5 alloy, in which Li ions are inserted into the Cu_6Sn_5 structure to form $Li_xCu_6Sn_5$. Nanocrystalline Cu_6Sn_5 alloy demonstrated a much higher initial lithium storage capacity than that of the crystalline Cu_6Sn_5 .

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References

- Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, Science 76 (1997) 1395–1399.
- [2] Y. Idota, US Patent 5, 478, 671 (1995).
- [3] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2943– 2948.
- [4] W. Liu, X. Huang, Z. Wang, H. Li, L. Chen, J. Electrochem. Soc. 145 (1998) 59.
- [5] J. Yang, M. Wachtler, M. Winter, O. Besenhard, Electrochem. Solid-state Lett. 2 (1999) 131–133.
- [6] O. Mao, R.L. Turner, I.A. Courtney et al., Electrochem. Solid-State Lett. 2 (1999) 3–5.
- [7] O. Mao, R.A. Dunlap, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 405–413.
- [8] O. Mao, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 414-422.
- [9] O. Mao, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 423-427.
- [10] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, Electrochem. Solid-State Lett. 2 (1999) 307–309.
- [11] Traces Program, Diffraction Technology Pty. Ltd., Australia.
- [12] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2045.