Research of Co-Sn alloy as Anode material for lithium ion battery

Wenhua Zhang1,3,*, Ping Liu2, Xingwang Zhang1,3, Zhizhao Ouyang1,3

1Nanchang Institute of Technology, Nanchang, China
2State grid of Jiangxi electric power research institute, Nanchang, China
3Nanchang Institute of Technology, Jiangxi Province Key Laboratory of Precision Drive and Control, Nanchang, China

*Corresponding author e-mail: zhangwenhua_610@163.com

Abstract. The CoSnx alloys with different atom ratio (x=2, 4, 8) were prepared by solid phase reduction reaction through mechanical ball milling. The structure and morphology were represented by X - ray diffraction (XRD) and scanning electron microscopy (SEM). the electrochemical performance of the alloy as anode material of li-ion battery was investigated by assembling the analog battery. The experimental results reveal that the nanostructured amorphous CoSn4 shows a relatively high initial discharge capacity (430 mAh/g) and good cycling performance, as its capacity still maintain at 360 mAh/g after the 15th cycle, with a capacity retention ratio of 84 %.

Key words: mechanical ball milling, CoSn2 alloy, Li-ion battery, anode materials.

1. Introduction

Lithium ion battery has become an ideal power source for advanced portable electronic products due to its high specific energy. Graphite is always the first choose for the negative pole of lithium ion battery. However, The most critical problem of graphite material is its lower theoretical capacity (372 mAh/g). As a result, the energy density of the battery is limited. Therefore, it is necessary to seek a higher li-insertion anode material. Due to high theoretical capacity and high vibration density, metal and metal alloy are considered to be another choice of cathode materials for li-ion batteries. For example, the maximum theoretical capacity of Sn is 990 mAh/g.

However, one of the biggest obstacles to the commercial application of the negative electrode of the alloy is that it will cause large volume changes in the charging and discharging process, which will lead to the pulverization of the material and the rapid attenuation of the capacity. In 1997, researchers from Fuji company found that the amorphous tin matrix composite oxide, because the amorphous network of the tin base composite oxide ACTS as a buffer medium, alleviates volume changes caused by alloying reaction, thus improving the electrode circulation performance[1]. However, the introduction of oxides not only improves the cycling performance, but also increases the irreversible capacity of the battery greatly due to the formation of Li2O. An effective solution is to form an intermetallic compound M'M. M 'is a non-reactive phase and does not react with lithium metal, and M is the active phase which realizing the extraction and insertion of lithium. Such intermetallic compounds include SnSb-C[2], Sn-Sb-Ni alloy[3], Cu6Sn5 alloy[3-5], Ni-Sn alloy[6,7], Sn-Fe-C system[8], and Sn-Mn-C system[9].
alloy phase Li\textsubscript{x}M'Sn is formed during the intercalation of lithium. It is also possible to form a mixed phase of Li\textsubscript{4.4}Sn with metal M', and the nonreactive M' provides a buffer matrix to reduce the volume change in the inner part of the electrode during displacement/intercalation of lithium and to maintain the integrity between particles and between the electrode sheet and the collector fluid.

Sn and Co can form a series of intermetallic compounds, such as Co\textsubscript{3}Sn\textsubscript{2}, CoSn and CoSn\textsubscript{2}. CoSn\textsubscript{2} alloy is also reported as a cathode material for Li-ion batteries\cite{10}. In this paper, CoSn\textsubscript{2}, CoSn\textsubscript{4} and CoSn\textsubscript{8} were prepared through solid phase reduction reaction during ball milling. The physical and chemical properties of the material were characterized by X-ray diffraction, scanning electron microscopy analysis and the electrochemical performance test of the simulated battery.

2. Experiment

2.1. The preparation of CoSn\textsubscript{x}

The ball mill used in the experiment is QM2ISP04 planetary ball mill (Nanjing university instrument factory), the ball grinding tank is 100 mL stainless steel ball grinding tank, and the reaction is conducted according to the ball material ratio 5:1 (mass ratio). The reactant: SnCl\textsubscript{4}·H\textsubscript{2}O (AR grade, National pharmaceutical group chemical reagent co., LTD.), CoCl\textsubscript{2}·4H\textsubscript{2}O (AR grade, Tianjin bodi chemical reagent co., LTD.), NaBH\textsubscript{4} (AR grade, National pharmaceutical group chemical reagent co., LTD.)

The solid phase reaction of the mixture of SnCl\textsubscript{4}·H\textsubscript{2}O and CoCl\textsubscript{2}·4H\textsubscript{2}O with molar ratios of 2:1, 4:1 and 8:1 was performed for 2 h by ball milling. Then, the distilled water was added to separate the pellets, and the black precipitate was obtained through filtration. After that, the distilled water was washed many times, and AgNO\textsubscript{3} solution was used to test the chloride ions. Finally, The required sample dry 60°C for 24 h in vacuum oven.

2.2. Electrochemical test

The prepared CoSn\textsubscript{x} alloy material is made into electrode sheet, which is composed of 80% alloy material, 5% acetylene black and 15% Teflon. The electrolyte is 1.0 mol /L LiPF\textsubscript{6} + EC/ DMC (EC: ethylene carbonate, DMC: dimethyl carbonate). Charging and discharging experiments were performed using the new battery test system (Shenzhen, Song he co., LTD.). The battery is discharged to 0.005V and charged to 1.500V at a constant current of 100mA/ g, and then repeated charging and discharging to test the capacity and circularity.

2.3. Determination of sample structure and morphology

The prepared samples were tested by X-ray diffraction (XRD) and electron scanning electron microscopy (SEM) to determine their structure and morphology. The XRD 26000 X-ray diffractometer is produced by Shimadzu, Japan. The KYKY23200 Electronic scanning electron microscope is produced by zhongke, Beijing.

3. Results and discussion

3.1. Structure and morphology of CoSn\textsubscript{x} alloy

Fig. 1 shows the XRD pattern of CoSn\textsubscript{x} alloy of different proportions. As shown in Fig. 1, when the atomic ratio for CoSn\textsubscript{2} and CoSn\textsubscript{4}, map display as amorphous, some weak broad peak (53° to 43°, 35°, 60°, etc.) corresponds to the CoSn\textsubscript{2} characteristic diffraction peaks of the crystal. When the atomic ratio is CoSn\textsubscript{8}, Strong diffraction peak appeared in 31 °, 33 °, 45 °, 55 °, 63 °, 65 °, corresponding to the elemental characteristics of diffraction peaks of the metal. It can be seen that as the content of Sn increases, the structure of the product changes from amorphous to crystalline state, which is mainly due to the formation of elemental tin by excessive Sn phase during the reduction process. Dahn et al. \cite{11} made a detailed study on the final crystal shape formed by different ratios of Sn and Co. They found that when the molar fraction of Co was between 28 % and 43 %, it was conducive to the formation of amorphous state, and because the amorphous structure was characterized by short-range order and long-
term disorder, the intercalation process of lithium could alleviate the stress between particles, prevent
the pulverization of materials, and improve the circulation performance of electrode materials. CoSn$_2$, CoSn$_4$ and CoSn$_8$ alloys are prepared in this paper. CoSn$_8$ cannot form amorphous phase, meanwhile, the materials of CoSn$_2$ and CoSn$_4$ exhibited amorphous characteristics. Therefore, the solid phase reduction method of ball grinding can be used to prepare CoSn$_2$ alloy, which is convenient for the preparation of amorphous CoSn$_2$ alloy. At the same time, without addition of water, the formation of metal boride can be reduced and the capacity of the material can be improved. While the reduction reaction is carried out at the same time as the mechanical ball-mill reaction, it can also promote the mixture of reactants and the dispersion of product particles, which is more conducive to the formation of amorphous particles.

![Figure 1. XRD pattern of CoSn$_x$ alloy of different proportions](image)

Fig. 2 shows the SEM images of the CoSn$_4$ alloy materials with the atomic ratio (the SEM images of the materials with three different ratios are similar). As can be seen from the Fig.2, the prepared material particles are very small (about 100 ~ 200nm), and the particles are clustered together. The surface of the product particles is fluffy and has rich pore structure, which will help the electrolyte to infiltrate into the particles better, increase the electrochemical reaction area, and improve the utilization rate and multiplier performance of the materials.
3.2. The electrochemical properties of CoSnx alloys

Fig. 3 shows the charge-discharge curves of CoSnx alloy materials with different atomic ratios in 1st cycle. E (V) represents the voltage relative to the Li+/Li reference electrode, and W (mAh/ g) represents the charge-discharge capacity. As shown, There is no obvious voltage platform for the lithium insertion reaction of CoSn2 alloy, while a voltage platform appears at 0.7v (vs.li+ / Li) during delithium process, which is similar to the CoSn2 alloy delithium platform reported in literature [12]. The lithium removal capacity of CoSn8 in 1st cycle was 590 mAh/ g, higher than that of CoSn4 (433 mAh/ g) and CoSn2 (323 mAh/ g) materials. This is because in CoSn2 alloy, Sn is the active lithium storage unit, while Co is the inert filler, which only serves as the substrate. For CoSn8 materials, the content of tin is high, so the capacity is large. It can also be seen from the charge-discharge curves of the three materials that the irreversible capacity of the three materials is relatively large in 1st cycle, and the reasons for this result may be as follows:1) The nanoparticles produced by ball mill have a larger surface area and higher activity, which promotes the irreversible reduction of electrolyte on its surface, 2) During the reaction, the change of pH value may lead to the formation of some oxides, which can react with Li irreversibly to form Li2O during the electrode reaction, 3) The formation of the electrode material will also cause irreversible capacity increase. In the future work, we should try to eliminate these adverse factors in the post-treatment of samples, such as reducing the irreversible capacity of materials by means of surface inactivation treatment and adjustment of pH value.
Figure 3. Charge-discharge curves of CoSnx alloys at different ratios in 1st cycle

![Charge-discharge curves of CoSnx alloys at different ratios in 1st cycle](image)

Figure 4. Cyclic properties of CoSnx alloys of different proportions

Fig.4 shows the cyclic performance of CoSnx alloys with different proportions. It can be seen that the lithium removal capacity of CoSn8 in 1st cycle is the highest, reaching 590mAh/g, but decreases rapidly with the increase of cycle times, in 10th cycle, the capacity was only 100 mAh/g, and the capacity retention rate was only 17%. The possible reason is that when the Sn content is too high, the amorphous state cannot be formed with Co in the reduction reaction process of ball-mill, and the amorphous state is precipitated in the form of simple tin, and the supporting structure is not formed with cobalt as the matrix, thus greatly reducing its circulation performance. As shown in Fig. 4, the cyclic performance of CoSn4 and CoSn2 is improved due to the amorphous structure. The lithium removal capacity of CoSn2 in 1st cycle was 323 mAh/g, and another 124 mAh/g after 15 cycles. CoSn4 showed better cyclic performance, with a lithium removal capacity of 430 mAh/g in 1st cycle and a capacity of 360mAh/g after 15 weeks, with a capacity retention rate of 84%. It can be seen that the cyclic performance of CoSn4 and CoSn2 with amorphous structure is significantly improved compared with that of CoSn8 with crystalline structure. The possible explanation is that the short-range order and long-range disorder of
amorphous materials show anisotropy in macroscopic properties. Therefore, during the deintercalation process, the structure and electric field stress generated by the diffusion of lithium ions in the material body and the transfer of electrons in the material structure can be alleviated, which avoids the pulverization of materials in the circulation process and improves the cyclic stability of materials. At the same time, the inert metal cobalt as a matrix also plays a very good role in buffering volume changes. Therefore, the amorphous material with active-inactive structure can have better cyclic stability. CoSn₄ alloy has higher cyclic capacity due to its higher active component Sn.

4. Conclusion
In this paper, a series of CoSnₓ intermetallic compounds were prepared by solid phase reduction through ball grinding, in which Sn is the active material, which determines the capacity of the electrode material. As a buffer matrix, Co acts as a buffer volume change. The results show that the amorphous CoSn₄ and CoSn₂ have better cyclic performance, while the CoSn₄ alloy with higher content of tin maintains a high delithium capacity (430 mAh/ g) and has good cyclic performance, which is expected to become a practical carbon anode material.

Acknowledgements
This work was supported by the Scientific and Technological Research Project Foundation of Jiangxi Education Department [GJJ161121] , the National Natural Science Foundation of China [21603093] and the Scientific and Technological Research Project Foundation of Jiangxi Education Department [GJJ151132].

References
[1] Idota Y, Kubota T, Mat sufuji A, et al. Tin-Based Amorphous Oxide: A High-Capacity Lithium-Ion Storage Material [J]. Science, 1997, 276: 1395.
[2] Jusef Hassoun, Gaelle Derrien, Stefania Panero, A SnSb–C nanocomposite as high performance electrode for lithium ion batteries[J]. Electrochimica Acta, 2009, 54: 4441-4447.
[3] Srijan Sengupta, Arghya Patra, Mainul Akhtar, Karabi Das, et al. 3D microporous Sn-Sb-Ni alloy impregnated Ni foam as high-performance negative electrode for lithium-ion batteries [J]. Journal of Alloys and Compounds, 2017, 705: 290-300.
[4] Xia Y Y, Sakai T, Fujieda T, et al. Flake Cu-Sn Alloys as Negative Electrode Materials for Rechargeable Lithium Batteries [J]. J Electrochem Soc, 2001, 148: 471.
[5] Wang Ke, He Xiangming, Wang Li, et al. Preparation of Cu6Sn5-Encapsulated Carbon Microsphere Anode Materials for Li-Ion Batteries by Carbothermal Reduction of Oxides [J]. J Electrochem Soc, 2006, 153 (10): 1859-1862.
[6] Ehrlich G M, Durand C, Chen X, et al. Metallic Negative Electrode Materials for Rechargeable Nonaqueous Batteries [J]. J Electrochem Soc, 2000, 147 :886.
[7] Lee H Y, Jang S W, Lee S M, et al. Lithium Storage Properties of Nanocrystalline Ni3Sn4 Alloys Prepared by Mechanical Alloying [J]. J Power Sources, 2002, 112: 8.
[8] Mao O, Dunlap R A, Dahn J R. Mechanically Alloyed Sn-Fe(-C) Powders as Anode Materials for Li-Ion Batteries. [J]. J Electrochem Soc, 1999, 146: 405.
[9] Beaulieu L Y, Dahn J R. The Reaction of Lithium with Sn-Mn-C Intermetallics Prepared by Mechanical Alloying[J]. J Electrochem Soc, 2000, 147: 3237.
[10] Zhang Jingjun, Xia Yongyao. Co-Sn Alloys as Negative Electrode Materials for Rechargeable Lithium Batteries [J]. J Electrochem Soc, 2006, 153 (8): 1466-1471.
[11] Dahn J R, Mar R E, Abouzeid A. Combinatorial Study of Sn1-xCox (0 < x < 0.6) and [Sn0.55Co0.45] 1+y Cₓ (0 < y < 0.5) Alloy Negative Electrode Materials for Li-Ion Batteries [J]. J Electrochem Soc, 2006, 153 (2): 361-365.
[12] Tamuraz N, Kato Y, Mikami A. Study on Sn-Co Alloy Anodes for Lithium Secondary Batteries [J]. J Electrochem Soc, 2006, 153 (8): 1626-1632.