Contents lists available at ScienceDirect





Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Carbon-coated copper-tin alloy anode material for lithium ion batteries

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ARTICLE INFO

Article history: Received 28 October 2008 Received in revised form 22 November 2008 Accepted 25 November 2008 Available online 13 December 2008

Keywords: Copper-tin alloy Carbon coating Anode material Lithium ion battery

ABSTRACT

Carbon-coated copper-tin alloy powders were prepared by heating of mixtures of thermoplastic poly(vinyl alcohol) and nano-sized copper-tin alloy particles in argon atmosphere. The products were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The electrochemical properties of the carbon-coated copper-tin alloy powders as anode materials for lithium batteries were studied by cyclic voltammetry (CV) and galvanostatic method. The anode showed high charge capacity up to 460 mAh g⁻¹ and stable cyclic performance even after 40 cycles. This could be ascribed to the existence of inactive matrix Cu which buffered the large volume change in the course of Li–Sn alloying–dealloying process, and the presence of carbon layer of alloy particles which enhanced dimensional stability during Li–Sn alloying–dealloying electrochemical process.

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1. Introduction

Due to great demand on high specific energy density and safety of the lithium ion battery for diverse application, considerable efforts have been made to explore different types of materials to be employed as anode materials [1-4]. Among them, tin-based materials have been widely studied as alternative anode materials to carbon for lithium ion batteries, because 4.4 Li atoms can react with Sn to deliver a specific capacity of 993 mAh g⁻¹. However, a large specific volume change usually occurs during the charging and discharging processes [5], which leads to rapid pulverization of the electrode [6,7] and decrease of electrical conductivity between active material particles. As a result, these alloy materials exhibit poor cycle performance.

It is believed that pulverization effects may be reduced by using smaller active particles and by using multi-phase systems or alloys [8,9]. The active/inactive nano-composite concept has been particularly investigated [10]. The concept involves the intimate mixture of two or more materials, one (e.g., Sn) electrochemically reacting with lithium, whereas the others act as electrochemically inactive confining buffers to accommodate the large volume change which accompany the electrochemical process [11]. It has been demonstrated that active/inactive nano-composite materials exhibit longer cycleability than that of pure tin electrode. However, capacity fading of the active/inactive nano-composite materials is inevitable [12]. Therefore, keeping or enhancing their dimensional stability during cycling is the most critical factor in solving the problem.

In this study, nanometer copper-tin alloy particles were encapsulated by amorphous carbon layer through carbonization of poly(vinyl alcohol) (PVA) at high temperature. The amorphous carbon layer can enhance dimensional stability of copper-tin alloy particles during Li–Sn alloying–dealloying electrochemical process. Hence, the anode exhibit good cycling performance.

2. Experimental

2.1. Preparation of nano-sized Cu–Sn alloy powders and carbon-coated Cu–Sn alloy powders

Nano-sized Cu–Sn alloy powders were synthesized by reductive precipitation of metal chlorides from aqueous solution with NaBH₄. To produce the Cu₆Sn₅ alloy powders, SnCl₂·2H₂O, CuCl₂·2H₂O and C₆H₅Na₃O₇·2H₂O were mixed together with molar ratios of 1:1.2:3.2, and solved in distilled water to form a 0.2 M solution of Sn²⁺. The solution was added drop-wise to 0.4 M alkalineNaBH₄ aqueous solution under strong magnetic stirring at room temperature. The superfluous NaBH₄ solution was used to ensure a complete reduction of the metal ions. After coprecipitation, the copper–tin alloy powders in the aqueous solution were aged 6 h in water bath with a constant temperature of 80 °C [13]. Then, the solution was used to solution temperature of 80 °C [13].

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tion was filtered and the product was washed thoroughly using distilled water and acetone three times, respectively. The black product was dried at 105 °C for 24h under vacuum. To encapsulate the copper-tin alloy nano-particles with the amorphous carbon, 2g poly(vinyl alcohol) was dissolved in distilled and deoxygenated water (40 ml) under magnetic stirring at 60 °C until a clear solution was observed. The nano-sized copper-tin alloy powders (0.4g) were dispersed in the solution. Then the viscous fluid was sent into electric tube furnace under argon atmosphere and heated up to $900 \,^{\circ}$ C. It was then held for 6 h (heating rate to the programmed temperature was $5 \,{}^\circ C \min^{-1}$ and a flow rate of Ar gas was 60 ml min⁻¹). Thus the carbon-coated copper-tin alloy powders were obtained. The crystal structure of obtained materials was detected by X-ray diffraction (D/adv-8) with Cu-K radiation. The morphology and microstructure of the powders were observed by field-emission scanning electron microscopy (FE-SEM: JSM-6700F) and transmission electron microscopy (H-800). The content of carbon was determined from the ignition loss of the sample heated at 900 °C for 1 h in air in a TGA apparatus.

2.2. Cells assembling and electrochemical test

Composite electrodes were prepared by pasting a slurry, which consists of 80 wt.% Cu–Sn alloy powder, 10 wt.% acetylene black and 10 wt.% LA132 binder (aqueous emulsion containing a copolymer of acrylamide, AM; lithium methacrylate, LiMAA; acrylonitrile, AN) dispersed in de-ionized water, onto a copper foil substrate. The electrodes were dried in a vacuum oven at $105 \,^{\circ}$ C for 24 h prior to use. Test cells were assembled in an argon-filled glove box using Celgard2400 as the separator, $1 \, \text{mol} \, l^{-1} \, \text{LiPF6}$ /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 BT-2000 battery tester at a constant current density of 50 mAg⁻¹ between 0.0 V and 2.0 V. Cyclic voltammetry measurements were initially conducted at a scanning rate of 0.5 mV s⁻¹ over the potential range from 2.00 V to 0.00 V on the Arbin BT-2000 battery tester.

3. Results and discussion

3.1. Morphology and structure of samples

Fig. 1 presents SEM and TEM pictures of nano-sized Cu-Sn alloy powders and their carbon-coated particles. In Fig. 1(a), irregular particles (about 30 nm) and their agglomerates can be observed. Fig. 1(b) shows Cu–Sn alloy particles with about 40 nm in size are dispersed homogeneous in amorphous carbon. From Fig. 1(c), it can be seen there is a distinct contrast difference in the image, which confirms existence of two phases, amorphous carbon and copper-tin alloy particles which indicates the copper-tin alloy particles are coated by amorphous carbon layer. The content of carbon in the carbon-coated sample can be determined by TGA results. TGA results of the sample are displayed in Fig. 2, which shows the weight loss of the powder terminated at about 600 °C. The weight loss below 600 °C is mainly due to the carbon in the powder. It can be assessed that carbon content in the powder is about 30% in mass. With temperature increasing up to 900°C, TGA shows the weight of the powder increased slightly, which may correspond to the oxidation of Cu-Sn 3 alloy.

Fig. 3 shows XRD patterns of the as-prepared nanometer Cu–Sn alloy and carbon-coated nanometer Cu–Sn alloy particles. The diffraction pattern of nano-sized Cu–Sn alloy powders synthesized by reductive precipitation method consists of two phases:



Fig. 1. SEM images of nano-sized Cu-Sn alloy (a), carbon-coated nano-sized Cu-Sn alloy (b) and TEM images of carbon-coated nano-sized Cu-Sn alloy (c).



Fig. 2. TGA curve of carbon-coated Cu-Sn alloy power.

the major phase of Cu_6Sn_5 and the impure phase of Cu_3Sn . But another impure phase of SnO_2 appears in carbon-coated powders, indicating that there was some oxidization in carbon coating process.

3.2. Electrochemical performance of carbon-coated nanometer Cu–Sn alloy particles

To investigate the electrochemical properties, cyclic voltammetry measurements were first conducted at a scanning rate of 0.5 mV s⁻¹ over the potential range from 2.00 V to 0.00 V. The initial five scanning cycles are shown in Fig. 4. From Fig. 4(a), it can be seen that, during the first scanning cycle, there are two reduction peaks and two oxidation peaks. The first reduction peak in the potential range 0.5-1.0 V is ascribed to the formation of solid electrolyte interface (SEI) film on the surface of electrode [14], which disappears in subsequent cycles; the second reduction peak close to 0.0 V versus Li/Li^+ is attributed to the formation of Li_{44} Sn. From Fig. 4(b) it can be seen that the shape of curves is almost similar to that in Fig. 4(a)except that the fourth scanning cycle and the fifth are nearly overlapping, indicating that the carbon-coated nano-sized Cu-Sn alloy electrode shows better cycling performance. From the second scanning cycle, the reduction peak close to 0.0 V versus Li/Li⁺ divides into two peaks, corresponding to two processes: lithium ions inserting Cu₆Sn₅ to form Li₂CuSn (0.4–0.2V) and further formation of



Fig. 3. XRD patterns of nano-sized Cu-Sn alloy and carbon-coated nanometer Cu-Sn alloy particles.



Fig. 4. Cyclic voltammetry profiles of nano-sized Cu–Sn alloy (a) and carbon-coated copper-tin alloy (b).

 $Li_{4,4}Sn (0.2-0.0V)$. This is in accordance with the result of Guo et al. [15].

Fig. 5 presents the discharge and charge profiles of nano-sized Cu–Sn alloy and carbon-coated nano-sized Cu–Sn alloy composite electrodes for the 1st, 20th, and 40th cycles.

In the discharge curve, 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 film formation, discharge voltage above 0.2 V is attributed to lithium ions insert in Cu₆Sn₅ to form Li₂CuSn, while discharge voltage between 0.0V and 0.2V corresponds to the formation of the fully lithiated Sn phase (i.e., $Li_{44}Sn$). In charge curve, the charge plateaus at about 0.5 V and 0.8 V correspond to the reversibly formation of the Li₂CuSn and Cu₆Sn₅, respectively [16]. A plateau at 0.1 V which does not appear in Cu-Sn alloy electrode, appears in the charge curve of the carbon-coated Cu-Sn alloy electrode. It is possible that the amorphous carbon coating layer affects the overall change in phase-change rate. Significant difference among voltage curves can be seen in Fig. 5(a), indicating that capacity fading happens in cyclic process. From Fig. 5(b), though the initial charge capacity is far less than the initial discharge capacity, the 20th and 40th charge and discharge curves almost overlap, showing that there is no obvious capacity fading in the following cycles. There is high irreversible capacity at the first recharge. It can be attributed to two main reasons. The one is the formation of SEI film on the surface of electrode which is inevitable. The second is the initiation of SnO₂ in carbon coating process and previous stud-



Fig. 5. Voltage profiles of copper-tin nano-particles (a) and carbon-coated copper-tin alloy particles (b).

ies have shown that SnO_2 led to high irreversible capacity at the first recharge [17]. In this study, the initial high irreversible capacity can be minimized by modifying the carbon coating process, such as increasing vacuum degree of oven, using more pure protecting gas.

Fig. 6 shows cycling performance and coulomb efficiency of the two samples. In Fig. 6(a), the first discharge and charge capacity of the nano-sized Cu-Sn alloy electrode is 620 mAh g⁻¹ and 450 mAh g⁻¹, respectively. Further cycling leads to a rapid capacity decay to 56 mAh g^{-1} after 40 cycles. It can be seen that the coulomb efficiency of the nano-sized Cu-Sn alloy powder in initial cycles is low, only 70% for the first cycle and reaching 97% till to the 20th cycle. Although the existing of inactive matrix Cu can buffer the large volume change in the course of alloying process, quick fading still happens. In contrast, in Fig. 6(b), the first discharge and charge capacities of the carbon-coated Cu-Sn alloy particle electrode are 1015 mAh $\rm g^{-1}$ and 600 mAh $\rm g^{-1}$, respectively. And after 40 cycles, there is 460 mAh retention. Columbic efficiency for carboncoated Cu-Sn alloy particles increases rapidly at the second cycle and then gradually with increasing cycle number, tends to saturate to about 98%. This high performance of carbon-coated Cu-Sn alloy powders is supposed to attribute to the presence of carbon layer of alloy particles, which enhances dimensional stability during Li-Sn alloying-dealloying electrochemical process. So, the cyclic performance of the carbon-coated Cu-Sn alloy powders is superior to the Cu–Sn alloy systems. This aspect, which may rise some concern on



Fig. 6. Cycle performance and columbic efficiency curves of nano-sized copper-tin alloy (a) and its carbon-coated powders (b).

the cycling columbic efficiency of the electrode, is under additional investigation.

4. Conclusion

Carbon-coated copper-tin alloy powders were prepared by heating of mixtures of thermoplastic poly(vinyl alcohol) and nanosized copper-tin alloy particles in argon atmosphere. Despite the inactive matrix Cu which buffers the larger volume change in the course of Li–Sn alloying–dealloying process, the external carbon layer of coated particles can enhance dimensional stability during Li–Sn alloying–dealloying electrochemical process. So, this material shows excellent capacity retention, 460 mAh g⁻¹ retention after 40 cycles. The carbon-coated Cu–Sn alloy powders have great potential as anode materials for improving the energy density of lithium secondary batteries.

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