Carbon-coated SbCu alloy nanoparticles for high performance lithium storage

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A B S T R A C T

In this study, carbon-coated SbCu alloy nanoparticles are synthesized via a facile preparation route in high-boiling point solvent. The structure and morphology of carbon-coated SbCu nanoparticles are characterized by scanning electron microscopy, transmission electron microscopy, elemental analysis, X-ray diffraction and Raman spectroscopy, revealing that the obtained particles are composed of intermetallic Cu_2Sb and Sb nanocrystallites coated with amorphous carbon. The core shell SbCu/C nanoparticles exhibits excellent performance when employed as anode. The first discharge capacity is 751 mAh g^{-1} and the initial coulomb efficiency is as high as 71.4%. Capacity fading is very small after 150 lithiation/delithiation cycles, retaining a stable reversible capacity of ~477 mAh g^{-1}. Moreover, it has a remarkable capacity retention of 87% at a current charge rate of 1C, which is far superior to large size carbon-coated SbCu particles and pure Sb particles prepared under different conditions.

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1. Introduction

Lithium-ion batteries (LIBs) play an indispensable role in portable electronic devices, electric vehicles and even large-scale stationary storage, owing to their exceptional advantages such as high energy and long service life. The most successful anode material in commercial LIBs is graphitic carbon, but it has the drawbacks of limited energy capacity (372 mAh g^{-1}), low tap density (<1 g cm^{-3}) and safety problem caused by low reaction potential (<0.1 V *vs.* Li/Li$^+$) [1—4]. Obviously, it could not satisfy the demand for high-energy density, lightweight and safety in next-generation electronics devices and vehicles.

Metal and alloy materials that can react with one or more lithium atoms/ions have attracted enormous attentions in the past decades, owing to high reversible capacities (*e.g.*, Li$_{4.4}$Sn, 990 mAh g^{-1}; and Li$_3$Sb, 660 mAh g^{-1}) [5,6]. Some of these materials, like Sb, also have high potentials versus lithium (Li/Li$^+$), which are helpful for suppressing Li dendrite growth on electrodes and thereby mitigating safety risks. However, large volume change (up to 390 vol%) during lithiation-delithiation process causes severe mechanical strain and pulverization of active materials, thus seriously

hindering their practical applications [7—9].

A lot of research efforts have been made in order to alleviate this problem, including (a) nanosizing; (b) intermetallic alloying; (c) reinforcing materials. The reduction of material dimensions into nanoscale as well as development of nanoscale architectures prove to be excellent method for enhancing the cycling performance of metal anodes, as evidenced by 10—20 nm Sb nanocrystals [10] and 20 nm hollow Sb nanoparticle [11]. After nanosizing, low dimensional Sb materials with high surface to volume ratio show significant reduction in stress generation and therefore lead to delayed cracking/pulverization and a long cycle life. However, nanoparticle agglomeration over discharge-charge cycling partially affects the benefit. As previously reported, intermetallics alloy, like Cu_2Sb [12,13], NiSb [14], $FeSb_2$ [15], which are typically composed of an active metal and an electrochemically inactive element, demonstrate significantly improved cyclability over pure metal. During the discharge process, lithium is incorporated intermetallic to form Li$_3$Sb along with the extrusion of inactive element. Conversely, Li ion is extracted from electrode and inactive element is readmitted under charging process. As inactive element and Li atom alternatively occupy the lattice site of alloy, the volume change of alloy during lithiation/delithiation process is much smaller than that of metal, hence providing a significant performance improvement on cycling stability. It is also widely accepted that the development of composite system via incorporation of carbon materials or

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electrochemically inert ceramics, for example, Sb-C [16,17], FeSb$_2$/Al$_2$O$_3$/C [18] and Sb/Cu$_2$Sb/C nanocomposite [19], could improve lithium storage performances by suppressing the volume change of metal anode active materials. These reinforcing materials with high toughness, if uniformly distributed, can act as barriers to prevent agglomeration, extending the benefits of small-scale active materials.

The present research focusses on facile synthesis of carbon-coated SbCu alloy nanoparticles with combined characteristics for enhanced cycling performance and high rate capacity. The structure and morphology are characterized and their relationships with electrochemical behaviors are investigated. Moreover, the possibility of exploiting the carbon-coated SbCu nanoparticles as a high-performance lithium anode is discussed.

2. Experimental section

2.1. Sample preparation

The synthesis of carbon-coated SbCu alloy nanoparticles was carried out in a three-necked flask and protected with argon at a constant flow rate of 50 mL/min through two gas nozzles [20]. Triethylene glycol (TEG) with high viscosity (10.3 cP @ 60 °C) and high boiling temperature (288 °C) was used as a stable organic solvent for chemical reactions. Two kinds of surface stabilizers, poly (vinylpyrrolidone) (PVP, MW = 360 000) and poly-(2-ethyl-2-oxazoline) (PEtOx, MW = 50 000), were utilized to protect particles.

First, 0.628 g SbCl$_3$, 2.0 g PVP, 0.45 g PEtOx and 150 mL TEG were dissolved in a flask that immersed in an oil bath preheated to 90 °C. Then, 1 g NaBH$_4$ dissolved in 80 mL TEG was dropwise added while the solution was stirred rapidly with a magnetic stirrer. The solution transformed into a black colloid in half an hour which indicates formation of Sb particles. Subsequently, the temperature was elevated up to 170 °C, and 20 mL TEG solution containing 0.15 g CuCl$_2$ was pipetted into flask followed by a ripening period of 90 min to produce SbCu nanoparticles. Finally, 1.5 g sucrose was added into the solution above. The added sucrose decomposed completely at an elevated temperature of 200 °C for 2 h, forming a carbon shell layer on SbCu nanoparticles. For comparison, large size carbon-coated SbCu particles and Sb particles were prepared by raising reduction temperature to 170 °C before addition of NaBH$_4$.

2.2. Materials characterization

XRD is a powerful technique widely used for studying the microstructure, phase identification, and compound analysis of materials. The phase structure of the as-prepared nanoparticles was determined using Philips X′ Pert Pro X-ray diffractometer with a Cu–Kα radiation, scanned at 0.02°/s in 2 theta range from 20° to 80°. Observations of powder morphology were conducted on a Hitachi S-4800 SEM. The applied voltage was 15 kV while the working distance was 10 mm. High resolution transmission electron microscope (HRTEM) images were obtained by Tecnai F30 microscope. Raman experiments were performed on the sample surface using LabRam I (Dilor, France) using 632.8 nm excitation line from a He-Ne laser with a laser power about 1.2 mW.

2.3. Electrochemical tests

Test electrodes were prepared by spreading a slurry of 90% active materials and 10% polyacrylic latex binder (LA132) onto a copper foil. Same mass loading of ~1 mg cm^{-2} was employed for all electrodes in order to minimize the effect of the electrode thickness on electrochemical performance. The electrodes were then dried at

100 °C in a vacuum oven for 12 h and mechanically pressed to enhance the contact between active materials and current collector.

The electrochemical performance of carbon-coated SbCu nanoparticles and related materials were tested using CR2025-type coin cells with a multichannel battery test system (NEWARE BTS-610, Neware Technology Co., Ltd., China). Coin cells consisting of as-prepared composites as positive electrode, a Li metal foil as negative electrode, a membrane (celgard 2400) as separator material and LiPF$_6$ (1 M) in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by vol%) as the electrolyte was assembled in an argon-filled dry glove box. Galvanostatic charge and discharge were carried out at a constant current density of 0.1 A g^{-1} (roughly C/5) with a cut-off voltage of 0.01–1.5 V (versus Li$^+$/Li) at room temperature.

3. Results and discussion

The SEM image in Fig. 1(a) shows that the carbon-coated SbCu (called SbCu/C for short in figures) alloy nanoparticles are mostly spheres with outer diameter of approximately 25 nm. Energy dispersive X-ray spectroscopy (EDS) analysis of the sample in Fig. 1 (b) exhibits the weight percentages of Sb, Cu and C elements are 76.85%, 14.09% and 9.06% respectively. In contrast, the morphology of carbon-coated SbCu particles and pure Sb particles synthesized at high reduction temperature of 170 °C are larger (D ≈ 125 nm) and more irregular as illustrated in Fig. 1 (c) and (d).

Further examination using TEM clearly reveals the core shell structure of the carbon-coated SbCu nanoparticles as shown in Fig. 2(a–c). High resolution TEM (HRTEM) micrograph in Fig. 2(d) exhibits that the d-spacing values of adjacent lattice planes in nanoparticle are 0.61 nm and 0.22 nm, which agrees wells with (0 0 1)plane of Cu$_2$Sb (0.61 nm; JCPDS: 01-087-1176) and (1 1 0) of Sb (JCPDS: 01-085-1322) respectively. The results directly confirm the partial alloying of Sb particles due to the elemental substitution by Cu in high-temperature solvent. Amorphous carbon of roughly 2 nm in thickness is continuously curved to form shell layer outside spherical SbCu alloy particles. Such carbon shell would be expected to prevent agglomeration and pulverization of active nanoparticles during lithiation-delithiation process. Fig. 2(e) and (f) illustrate the big size and irregular shape of the carbon-coated SbCu particles and pure Sb particles synthesized at high reduction temperature of 170 °C. The lack of nano size effect in these materials possibly lead to large volume expansion and poor mechanical stability when working as anode for lithium-ion battery.

A schematic sketch of the formation of carbon coated SbCu alloy particles is illustrated in Fig. 3. Initial Sb nanoparticles are produced by chemical reduction in high temperature solution with the help of stabilizers. After the addition of copper salts, the Sb particles undergo site substitution and partial alloying to form binary phase Cu$_2$Sb. Finally, the Sb/Cu$_2$Sb alloy particles are wrapped with amorphous carbon layer of approximately 2 nm in thickness deriving from the carbonization of sucrose.

XRD was employed to study the phase structure of carbon-coated SbCu alloy nanoparticles as well as large-size carbon-coated SbCu particles and pure Sb particles reference samples. The XRD patterns in Fig. 4(a) show that the as-prepared carbon-coated SbCu sample consist of two phases. The first group of peaks at 8.7°, 40.1°, 41.9°, 51.6°, 59.4°, 65.9°, 68.5° are attributed to metal Sb (JCPDS: 01-085-1322), while another group of peaks at 26.619°, 34.9°, 31.6°, 43.5°, 45.3° are consistent with the standard card of Cu$_2$Sb alloy (JCPDS: 01-087-1176). Generally, the width of XRD peaks is greatly related to the crystallite size according to Scherrer formula. The relative broad peaks clearly confirm the particles are in the small diameter range. In contrast, the carbon-coated SbCu and pure Sb reference samples synthesized through high