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Sb-Al_xC_y-C Nanocomposite Alloy Anodes for Lithium-Ion Batteries

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ABSTRACT

We present a facile approach to making Al-Sb, carbon-modified (Al-Sb-C) nanocomposites for use as new anode materials in lithium-ion batteries (LIB). Alloying is achieved by one step synthesis using high energy mechanical milling (HEMM), producing nanometer-sized alloy particles of Sb-Al_xC_y-C. Based on electrochemical analyses, we determined that Sb acts as an active material, and both Al and carbon create a hybrid buffering matrix that mitigates the volume expansion of the active material during lithiation/delithiation to a greater degree than that by a pure metallic matrix (AlSb). In addition, we optimized the stoichiometric ratio of Al and Sb with regard to specific capacity and cycling performance. Of the ratios tested, a 1:1 molar ratio of Al and Sb exhibited the best cycling performance (302.5 mAh g^{-1} after 200 charge/discharge cycles). Although our Al-Sb-C composite had low initial coulombic efficiency (~59%), recovery to ~97% occurred within three cycles, indicating that initial side reactions are quickly reduced over the course of cycling. AlSb-C anodes also showed good rate capability and volumetric capacity. Overall, the new AlSb-C composite is a promising candidate for use as negative electrodes in lithium-ion batteries, providing an alternative to commercially available graphite electrodes.

1. Introduction

Lithium-ion batteries (LIBs) are some of the most commonly used energy storage devices worldwide. They are widely used in portable electronic devices, hybrid electric vehicles (HEVs), and stationary storage applications [1–3]. Over the last few decades, much research to find materials that enhance device-battery performance in terms of capacity, rate capability, and lifetime has been carried out. In particular, the development of new anode materials for LIBs is very important, allowing the development of the next generation of high-performance LIB devices.

Currently, graphite (372 mA h g^{-1}) is the most used anode in commercial LIBs; however, many candidate materials that form lithium compounds have been suggested as alternatives. These alternatives include Sn- [4–7], Sb- [8,9], P- [10,11], and Zn-based [12–14] alloys because they have high theoretical capacities, i.e., 990, 660, 2596, and 410 mA h g^{-1}, respectively. The high capacities of these composites are associated with the accommodation of a large number of Li ions with the corresponding metal atoms (e.g., $Li_{4.4}Sn$ and Li_3Sb, etc.) [15]. Nevertheless, these materials generally suffer from cycling instability during charging and discharging because of the large volumetric changes that occur upon lithiation/delithiation, one consequence of which is the crumbling of alloy particles [1–3].

Numerous different approaches have been proposed to overcome this volumetric change problem in alloys used as anodes. Among these, the use of metallic/intermetallic alloy compounds consisting of an active material and inert metal along with an amorphous carbon matrix has been shown to improve the cycling behavior of anode materials with those of pure metals[16–19]. In these approaches, although the overall capacity is reduced as the ratio of inert metal increases, both cycling stability and rate capability are significantly improved. The improvement occurs because the inert

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metal is not only capable of reinforcing the matrix by absorbing mechanical strain upon lithiation, the inert matrix forms conductive pathways in-between active materials. Recently, further research based on this principle has demonstrated the superiority of incorporating inactive metals into the carbon matrix (e.g., Cu_2Sb, Mo_3Sb_7, NiSb, FeSb, etc.) [15,16,20–24].

In this report, we present a new nanocomposite alloy composed of AlSb-C as an anode electrode material. The Sb nanoparticles were well-mixed in a hybrid matrix of Al and carbon (Al_xC_y-C) by high-energy mechanical milling (HEMM). During HEMM, the micrometer-sized Al particles create the secondary matrix, forming a nanocomposite with the amorphous carbon matrix. This synergistically prevents the aggregation of Sb nanoparticles. By varying the atomic ratio of Al and Sb, an optimal ratio was experimentally determined based on monitoring of electrochemical performances. We demonstrate that the optimized AlSb-C composite has excellent cyclability and rate capability along with a high tap density.

2. Experimental

2.1. Preparation of AlSb-C Nanocomposites

Mixtures of Al (7–15 μm, 99.5%, Alfa Aesar) and Sb (100 mesh, 99.5%, Aldrich) powders at stoichiometric ratios of 1:1, 1:2, and 2:1 were manually ground in a mortar. Subsequently, 30 wt.% carbon black-super P (Alfa Aesar, 99.99%) was mixed with the Al and Sb mixtures. The AlSb-C alloy composite was synthesized by high energy mechanical milling (HEMM) at a speed of 300 rpm 40 times for 1 h each time in a planetary ball mill (Pulverisette 5, Fritsch) at ambient temperature under an Ar atmosphere. Al, Sb, and carbon powders were placed into a zirconium oxide bowl (80 cm^3) with zirconium oxide balls (diameter 3/8″ and 3/16″) at a ball-to-powder ratio of 20:1.

2.2. Material Characterization

The crystalline structures of each sample were characterized by X-ray diffraction (XRD, D/MAX-2200 Rigaku, Japan). For ex-situ XRD measurement, a coin-type electrochemical cell was disassembled using two pliers (wolf looping pliers); one to hold the top half of the cell, and the other to remove the bottom part after 40 cycles of charge/discharge processes in an Ar-filled glove box. Then the electrode was taken out of the cell and rinsed with anhydrous dimethyl carbonate (DMC) to clean off the excess salt from the electrolyte. After drying the electrode sample, it was pasted on Kapton® tape. Finally, it was sealed with another Kapton film to avoid contact with air during XRD measurement. The morphology and composition of the synthesized alloys were examined by scanning electron microscopy (SEM, Hitachi S4700, Japan) and transmission electron microscopy (TEM, TECNAI G2F30). For ex-situ SEM, disassembly of the coin cell and cleaning of the electrode were performed as done in ex-situ XRD measurements after 100 cycles of charge/discharge processes. The electrode powder sample collected from a disassembled coin cell was observed under SEM.

2.3. Electrochemical Measurements

To prepare an anode electrode, a slurry was prepared by dispersing the active powder material (AlSb-C with an atomic ratio of 1:1, 1:2, and 2:1 for Al and Sb), carbon black (Super P, Aldrich), as a conductive component, and poly(vinylidene fluoride) (PVDF, average M_w of 534,000 by GPC, Aldrich) as a binder at a weight ratio of 70:15:15 in *N*-methyl-pyrrolidone (NMP). The slurry was well-mixed and cast on a Cu foil by the doctor blade method. The sample was then subjected to pressing and dried overnight at 70 °C in a vacuum oven. The mass loading of the electrode was about 2–3 mg cm^{-2}. Coin-type electrochemical cells were assembled in an Ar-filled glove box using a lithium foil as a counter electrode, polyethylene (PE) as a separator, and 1 M $LiPF_6$ in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 by v/v) as the electrolyte solution. The charge/discharge measurements were carried out galvanostatically over a voltage range of 0.0–2.0 V using a battery cycler (WBCS3000, WonAtech). Each cycle was defined as the loop of one charge/discharge process. The voltage of discharge started at 2.0 V and went down to 0.0 V at the fully discharged state. The following charge continued at this point of 0.0 V and reached 2.0 V at the fully charged state. Further cycles were carried out in the same manner. For volumetric capacity measurement, the tap density (g cm^{-3}) of the as-prepared AlSbC was calculated from the measurement of the volume and weight for the AlSbC powder. To do so, the AlSbC powder was filled to 0.5 ml in a cylindrical container and the weight was measured. The ratio of this powder weight and volume (0.5 ml) determined the tap density of the as-prepared AlSbC powder. The volumetric capacity (mAh cm^{-3}) was obtained using this tap density (g cm^{-3}) and the specific capacity (mAh g^{-1}) was measured. The rate-cycling performance of the cells was tested at different charge current densities of 100, 500, 1000, and 3000 mA g^{-1}.

3. Results and Discussion

3.1. Crystallography and microstructure of the as-prepared AlSb-C alloys

Fig. 1 shows the XRD patterns of the AlSb-C nanocomposites prepared at three different atomic ratios (1:1, 2:1, and 1:2) along with those of Al, Sb, and AlSb. The AlSb peaks were well-matched with those of AlSb and did not show the presence of other phases or impurities (PDF#06-0233), implying that mechanical alloying occurred during HEMM. Alloying of AlSb with carbon induced some changes in the crystallographic phases. For AlSb(1:1)-C and AlSb(2:1)-C, peaks (at ~28° and ~44°) remained, but other peaks disappeared due to the amorphous carbon matrix inserted in-between AlSbs. However, in the case of AlSb(1:2)-C, several sharp peaks (~39°, ~42°, ~52°, ~58°, ~66°, ~68°, and ~75°) appeared that were exactly overlapped with the Sb reference peaks. This indicated that the majority of Sb atoms existed independently in the nanocomposite after the HEMM process. This implies two possibilities: i) an excess amount of Sb did not

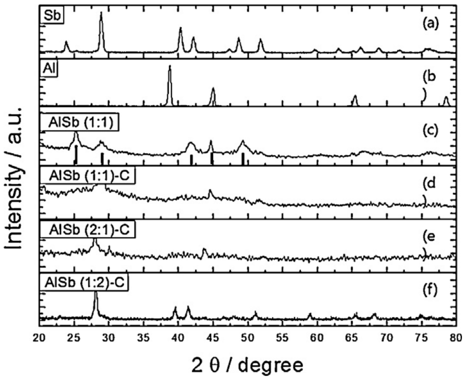

Fig. 1. XRD patterns of (a) Sb, (b) Al, (c) AlSb, (d) AlSb(1:1)-C, (e) AlSb(2:1)-C, and (f) AlSb(1:2)-C. The theoretical peak positions of AlSb alloy are shown under the XRD data in (c) as a reference.