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Large-scale synthesis of ternary Sn_5SbP_3/C composite by ball milling for superior stable sodium-ion battery anode

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ABSTRACT

Alloy-based materials (i.e. Sn, Sb, P) are promising candidates for sodium-ion battery (SIB) anodes, but they suffer from capacity decay during charge/discharge cycling due to the pulverization caused by their huge volume change. Nanostructures can slow down the capacity fade, but most of the synthesis methods of such nanostructured anodes are difficult to scale-up. Herein, a ternary Sn_5SbP_3/C composite was fabricated by a green, low cost, one-step and easily scalable ball-milling of elementary Sn, Sb, P, and C. The microstructure of the ball-milled powders consists of micrometric agglomerates of active nano Sn_4P_3 and SnSb and Sn particles. Carbon in the composite acts as a conducting matrix, and it does not only benefit to the ball milling efficiency, but also benefit to the cycle life of the electrode. Each of the active Sn_4P_3 and SnSb and Sn phases in the composite functions mutually as a buffer for the others. As a result, this ternary composite anode delivers a good capacity of 352 mA h g^{-1} at the current density of 2 A g^{-1}, which is notably higher than that of the binary Sn_4P_3/C and SnSb/C composites produced under the same conditions.

1. Introduction

Sodium-ion batteries (SIBs) have been attracting great interest recently due to the low cost and abundance of sodium resources, especially for applications in stationary energy storage [1–16]. The successful commercialization of SIBs does not only calls for the development of electrode materials with enhanced performance, but also scalable synthesis protocols [17]. Alloy-based materials are believed to be very promising candidates for SIB anodes due to their high gravimetric and volumetric capacities, and slightly higher thermodynamic potential [1,18,19]. For instance, group 14 (Sn, $Na_{15}Sn_4$, 847 mA h g^{-1}) and 15 elements (P, Na_3P, 2596 mA h g^{-1}; Sb, Na_3Sb, 660 mA h g^{-1}) based alloys [14,20,21] have been intensively studied recently and have showed promising properties. Nevertheless, large volume changes (>200%) are inevitable for these alloy anodes during sodiation/desodiation. The huge volume expansion will lead to continuous pulverization, particle cracking, and subsequent separation of the active materials from the current collector and result in fast capacity fade [1,2,22].

Nanomaterials with designed and optimized structures can slow down the capacity fade. The use of these nanosized materials by industry in the near future is unlikely, however, because of their complicated synthesis procedures, very high synthesis costs, high surface reactivity, low tap density, and difficulties for large-scale synthesis. In contrast, ball milling is a simple, cheap, and easily scalable synthesis method, and hence, it has a potential for industrial-scale application. Binary composite systems such as Sn_4P_3 and SnSb formed via ball milling have been shown to have significantly better electrochemical performance over pristine Sn, Sb, or P.[20–23] The electrochemical performance of the ball milled binary Sn_4P_3 or SnSb is still far from adequate for practical applications, however [23–26].

Herein, we report a ternary Sn_5SbP_3/C composite synthesized via ball-milling, which contains Sn_4P_3, SnSb and Sn nanoparticles (NPs), which are in intimate contact with each other and form heterojunctions in a conductive carbon matrix. The ternary composite displays superior electrochemical performance to the binary Sn_4P_3/C or SnSb/C composite. It was found that the Sn and SnSb in the composite facilitate the electron transfer and Sn_4P_3 provides high sodium storage capacity. The SnSb phase also promotes a superior stable cycling performance by the formation of an intermediate amorphous phase Na_xSb [23,27–29]. It seems that the superior electrochemical performance of the ternary

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Sn_5SbP_3/C composite is resulted from a synergetic effect of the multi phased nanostructure on a conductive network. Importantly ball milling is a scalable process and a large volume of composite architecture electrodes can be easily produced for practical applications.

2. Experimental Section

2.1. Preparation of Sn_5SbP_3/C ternary composite

Sn_5SbP_3/C powder was directly synthesized by ball milling the raw materials of Sn (Aldrich, ≥99.8%), Sb (Aldrich, ≥99.5%), red phosphorus (Aldrich, ≥99%) and carbon black. The weight ratio of Sn: Sb: P: C in the composite is 64.26:13.18:10.06:12.5. The ball milling was conducted in a planetary QM-1SP2 ball mill for 30 h at 500 rpm. A stainless steel jar and stainless steel balls of 10 mm in diameter are used. The powder-to-ball weight ratio was 1:30. For comparison, binary composites SnSb/C and Sn_4P_3/C were also synthesized under the same conditions. The weight ratios are Sn: Sb: C = 43.19: 44.31: 12.5 and Sn: P: C = 73.11: 14.39: 12.5 in the binary composites SnSb/C and Sn_4P_3/C respectively. The storage and handling of all the samples were performed in an Ar filled glovebox (MBraun Unilab).

2.2. Materials characterization

The phasic composition and information of the as-prepared powders were characterized by powder X-ray diffraction (XRD) on a GBC MMA diffractometer with a Cu K_α radiation at a scanning rate of $1^\circ\ min^{-1}$. The particle morphology and size of the prepared powder materials were characterized on a JEOL JSM-7500FA field-emission scanning electron microscope (FESEM) and on a JEOL ARM-200F cold field emission and aberration-corrected transmission electron microscope (TEM).

2.3. Electrochemical measurements

Electrodes were fabricated using a slurry-coating method. The synthesized materials (Sn_5SbP_3/C, Sn_4P_3/C and SnSb/C) were mixed with Super P carbon black and carboxymethyl cellulose (CMC) in the weight ratio of 8:1:1 to form slurry with deionized (DI) water. Then, the slurry was coated on copper foil and dried in a vacuum oven at 80 °C for 12 h. Coin-type (CR2032) cells were assembled in an argon-filled glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm), with 1 M $NaClO_4$ in a mixture of propylene carbonate (PC) with 5 wt. % fluoroethylene carbonate (FEC) as the electrolyte. Cyclic voltammetry (CV) tests were conducted on a Bio-logic VMP-3 electrochemical workstation at a scan rate of $0.05\ mV\ s^{-1}$. The cells were galvanostatically charged-discharged between 0.01 and 2.0 V versus Na/Na^+ at various current densities on a Land battery tester. The mass loading of active material (Sn_5SbP_3, Sn_4P_3 and SnSb) was over $0.78\ mg\ cm^{-2}$. The specific capacity was calculated based on the weight of pure Sn_5SbP_3, Sn_4P_3 and SnSb active materials.

3. Results and discussion

Fig. 1a presents the X-ray diffraction (XRD) patterns of the ternary Sn_5SbP_3/C and the binary Sn_4P_3/C and SnSb/C composites. The ternary Sn_5SbP_3/C composite contains three intermetallic and metallic phases: Sn_4P_3 (ICSD#15014), SnSb (ICSD#52303) and Sn (ICSD#40037). In contrast, only Sn_4P_3 or SnSb was observed in the binary composite Sn_4P_3/C or SnSb/C, respectively. The carbon black is not observed in the XRD patterns due to its amorphous features, but it can be clearly identified by Raman analysis, as shown in Fig. S1 in the Supporting information. Also, no bonds of C with Sn, Sb, and/or P are observed in X-ray photoelectron spectroscopy (XPS) analysis (Fig. S2). Fig. 1b presents the a Rietveld refinement profile for the Sn_5SbP_3/C composite, performed by using the GSAS-II software package [30]. All the peaks in the XRD pattern of the ternary Sn_5SbP_3/C can be indexed those of hexagonal Sn_4P_3 ($R\bar{3}m$), cubic SnSb ($F\bar{m}3m$), and tetragonal Sn ($I4_1/amd$). The lattice parameters obtained from the Rietveld refinement are $a = 4.0283$ Å, $c = 35.6999$ Å for the Sn_4P_3, $a = 6.1278$ Å for the SnSb and $a = 5.8456$ Å $c = 3.1903$ Å for the Sn respectively. The amount of each phase in the Sn_5SbP_3 was calculated as 65.75 ± 3.14 wt% Sn_4P_3, 18.54 ± 0.62 wt% SnSb, and 15.71 ± 0.67 wt% Sn.

The as-milled Sn_5SbP_3/C, Sn_4P_3/C and SnSb/C powders were characterized by SEM and the results are shown in Fig. 2. It can be seen that the powders in all three samples show irregular shapes in their morphology. The agglomerated and micro sized particles are the main constituent of the powders, and there are also numerous primary nanoparticles about 50 nm–100 nm in size (Fig. 2a–c). The mixed structure of the micro- and nano- particles may allow full contact of the electrolyte with the active materials and hence facilitate an efficient ion transportation [31]. It can also be seen that Sn, Sb, and P are distributed uniformly in the Sn_5SbP_3/C composite according to the energy dispersive X-ray spectroscopy (EDX) (Fig. 2d). EDX results for the Sn_4P_3/C and SnSb/C are shown in Fig. S3 and the compositions of the three different powders are listed in Table S1.

Fig. 3 shows a TEM image, and a HRTEM image taken from a micron particle of the Sn_5SbP_3/C composite. The micron particle is

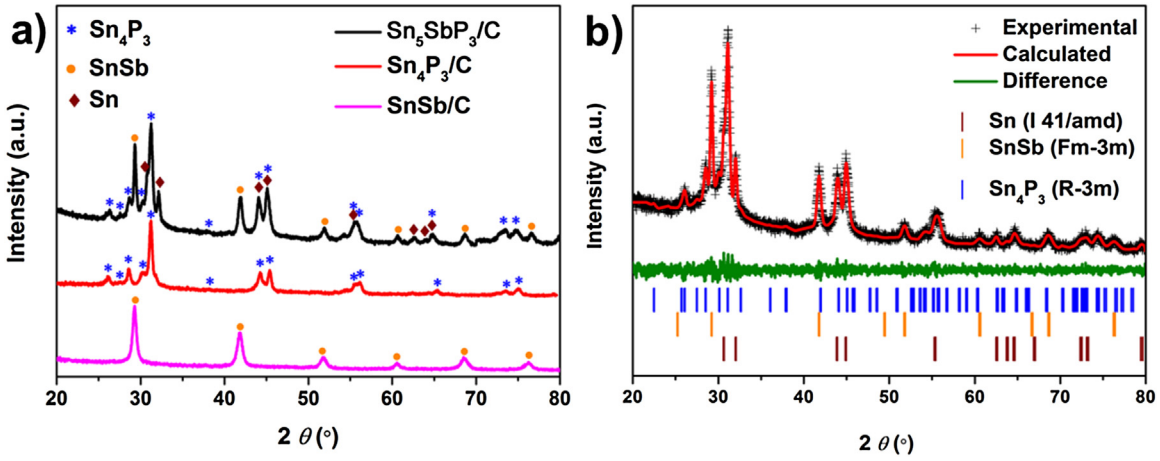

Fig. 1. a) XRD patterns of Sn_5SbP_3/C composite, Sn_4P_3/C and SnSb/C; b) Rietveld refinement profile for the Sn_5SbP_3/C composite.