



Iron-antimony-based hybrid oxides as high-performance anodes for lithium-ion storage

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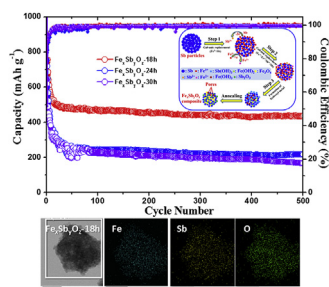
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HIGHLIGHTS

- Fe-Sb-based hybrid oxides are synthesized via galvanic replacement reaction.
- $\text{Fe}_x\text{Sb}_y\text{O}_z$ composites have nanoparticles consisting of crystalline Sb, Sb_2O_3 , and Fe_3O_4 .
- $\text{Fe}_x\text{Sb}_y\text{O}_z$ composites possess enough spaces functioning as buffers during lithiation.
- Formation of active and inactive phases leads to enhanced electrochemical performances.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a facile approach to synthesize Fe-Sb-based hybrid oxides nanocomposites consisting of Sb, Sb_2O_3 , and Fe_3O_4 for use as new anode materials for lithium-ion batteries. The composites are synthesized via galvanic replacement between Fe^{3+} and Sb at high temperature in triethylene glycol medium. The phase, morphology, and composition changes of the composites involved in the various stages of the replacement reaction are characterized using X-ray diffractometry, high-resolution transmission electron microscopy, and energy dispersive X-ray spectroscopy. The as-prepared composites have different compositions with very small particle sizes ($< < 10$ nm). The $\text{Fe}_x\text{Sb}_y\text{O}_z$ -18 h composite, for instance, exhibits high capacity, better cyclic stability, and rate performance than other composites, with a highly stable specific capacity of 434 mAh g^{-1} at 500 cycles. The excellent electrochemical performance can be ascribed to the high interfacial contact area between the nanocomposite and electrolyte, stable structure of the composites owing to a mixture of inactive phases generated by the conversion reaction between Li^+ and oxide metal—whose structure serves as an electron conductor, inhibits agglomeration of Sb particles, and acts as an effective buffer against volume change of Sb during cycling—and high Li^+ diffusion ability.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are one of the most commonly used energy storage devices worldwide including in portable

electronic devices, hybrid electric vehicles, and stationary storage applications [1–3]. Graphite has been widely used as the commercial anode material owing to its low cost, good conductivity, and electrochemical stability. However, graphite can no longer satisfy the demand

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for high energy density and power density in LIBs owing to the limited theoretical capacity of 372 mAh g^{-1} (LiC_6). Therefore, many candidate materials have been suggested as alternatives to determine new anode materials with enhanced capacities, improved rate capabilities, and prolonged cyclic life. Sn- (990 mAh g^{-1}) [4–7], Sb- (660 mAh g^{-1}) [8,9], P- (2596 mAh g^{-1}) [10,11], and Zn-based (410 mAh g^{-1}) [12–14] materials can be employed owing to their high theoretical capacities. However, the large volume expansion of these anode materials during the alloying process with Li^+ ions is a severe problem to overcome. Such significant volume change disintegrates the electrode material from the current collector and leads to the continuous depletion of the electrolyte owing to the regrowth of the solid electrolyte interface (SEI) film, resulting in the fading of capacity and the deterioration of cycle life [15,16]. Several materials, such as nanoalloys, active and inactive composite alloy materials, or intermetallic compounds (Cu_2Sb , InSb , SnSb , and AlSb), have been developed to overcome the aforementioned problem [17–21]. Among them, the nanostructured materials, which rely on the creation of short diffusion paths for Li^+ transport and free space to accommodate the large volume change, are one of the effective ways to enhance the electrochemical performance [22–28]. Although nanostructured materials can accommodate the mechanical strain of Li^+ alloying/dealloying much better than the bulk materials, the limited structural stability remains an obstacle. The subsequent approach is to synthesize active/inactive intermetallic compounds, in which an inactive metal (Co, Fe, Ni, Cu, ...) can serve as a buffer that partly alleviates the mechanical stress caused by the volume change of the active phase, acts as a barrier against the aggregation of active metal during Li^+ (de)alloying processes [15], and serves as an electrical conductor to enhance the electrical integration in the anode [29–33]. The incorporation of transition metal oxides as anodes involves Li^+ conversion reactions consisting of an electrochemically driven reversible decomposition of the oxide precursor (MO) into an $\text{M/Li}_2\text{O}$ nanocomposite. This process can release Li^+ upon the following charge, and Li_2O can act as an effective buffer against volume changes during the (de)alloying process [15,34,35].

Herein, we present a new approach to synthesize $\text{Fe}_x\text{Sb}_y\text{O}_z$ ($\text{Sb/Sb}_2\text{O}_3/\text{Fe}_3\text{O}_4$) nanocomposites as new anode materials for lithium-ion cells. The composites were synthesized via galvanic replacement between Fe^{3+} and antimony at a high temperature (180°C) in triethylene glycol medium. The composition and morphology of the composites can be controlled effectively by changing the experimental conditions such as reaction time, concentration of Fe^{3+} ions, and/or temperature via galvanic replacement reaction. Our composites were designed aiming at the following attributes: (i) particles with nanostructures to facilitate fast Li^+ diffusion and provide effective strain accommodation during volume expansion/contraction, (ii) an inactive phase to ensure improved electronic conductivity and serve as a buffer that partly alleviates mechanical stress, and (iii) enhanced integrity between the electrode material and current collector to ensure durable cycle life.

2. Experiment section

2.1. Synthesis of Sb nanoparticles

Sb nanoparticles were synthesized via chemical reduction. For the preparation of Sb nanoparticles, 0.70 g of polyvinylpyrrolidone (PVP, $M_w = 360,000$, Sigma-Aldrich) and 0.15 g of poly-(2-ethyl-2-oxazoline) (PEtOx, $M_w = 50,000$, Sigma-Aldrich) as surface stabilizers were dissolved in 30 mL of triethylene glycol (TEG, 99%, Sigma-Aldrich) with vigorous stirring at 90°C . When the solution was homogeneous, 30 mL of 0.10 M antimony chloride solution ($\text{SbCl}_3 \cdot 5\text{H}_2\text{O}$, 98%, Sigma-Aldrich) in TEG was added. After 20 min, 60 mL of 0.80 M sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich) in TEG was added to the solution in a drop-wise manner. Black Sb colloids were observed immediately. After complete addition, the mixed solution was stirred for another 2 h at 90°C under an argon atmosphere. Subsequently, Sb

nanoparticles were collected using centrifugation at 10,000 rpm for 15 min, and washed three times with ethanol solution after centrifugation. The Sb nanoparticles were suspended again and sonicated in 120 mL TEG until a homogeneous suspension was achieved. This solution was used for the synthesis of $\text{Fe}_x\text{Sb}_y\text{O}_z$ nanoparticles in the following stage.

2.2. Synthesis of $\text{Fe}_x\text{Sb}_y\text{O}_z$ nanoparticles

$\text{Fe}_x\text{Sb}_y\text{O}_z$ nanoparticles were synthesized by refluxing the obtained Sb nanoparticles and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%, Sigma-Aldrich) in 150 mL TEG at 180°C under argon atmosphere. Vigorous stirring was maintained throughout the synthesis. When Sb nanoparticles were fully dispersed in 120 mL of TEG, this solution was heated to 180°C . After 30 min, 30 mL of 0.048 M FeCl_3 solution in TEG was added drop-wise to the solution. Subsequently, the temperature was maintained constant at 180°C for the different reaction times of 18 h, 24 h, and 30 h. $\text{Fe}_x\text{Sb}_y\text{O}_z$ nanoparticles were obtained by centrifugation at 10,000 rpm for 15 min and washed with distilled water three times. Finally, the sample was dried in a vacuum oven at 70°C for 4 h, and thereafter annealed under argon atmosphere at 300°C for 4 h and collected. The final products are referred to as $\text{Fe}_x\text{Sb}_y\text{O}_z$ -18 h, $\text{Fe}_x\text{Sb}_y\text{O}_z$ -24 h, and $\text{Fe}_x\text{Sb}_y\text{O}_z$ -30 h.

2.3. Material characterization

The as-prepared samples were examined using X-ray powder diffraction (XRD, Japan) with an automated RIGAKU/DMAX2200 X-ray diffractometer with monochromatic $\text{Cu K}\alpha$ radiation and the 2θ Bragg angles were scanned over a range of 20 – 80° at a rate of $1.0^\circ/\text{min}$. The morphology of the powder samples was investigated using high-resolution transmission electron microscopy (HRTEM) images obtained from the JEM-2100F (JEOL) instrument. The composition of the samples was investigated using scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) with the JEM-2100F (JEOL) instrument.

2.4. Electrochemical measurements

The electrochemical performance was investigated directly using coin cells. For the measurements of the electrochemical performance, electrodes were prepared on Cu foils with slurries comprised of 70 wt% active material, 15 wt% Super P, 15 wt% polyvinylidene fluoride, and *N*-methyl pyrrolidone as the solvent. The electrodes were dried at 60°C for 3 h in an oven and at 120°C overnight in a vacuum oven. The cells were assembled in an Ar-filled glove box using a lithium foil as the counter electrode, polyethylene membrane as the separator, and 1 M LiPF_6 in ethylene carbonate/diethylene carbonate (1:1 in volume) as the electrolyte solution. The galvanostatic charge/discharge experiments were carried out at a constant current density of 100 mA g^{-1} at 0.01–2.00 V (vs. Li/Li^+) on a battery cycler (WBCS3000, WonAtech) system. The rate-cycling performance of the cells was tested at different charge current densities of 100, 500, 1000, and 3000 mA g^{-1} after 15 cycles. The electrochemical impedance spectroscopy (EIS) measurements were performed with ZIVE MP1 at an AC voltage of amplitude 10 mV in the range of 100 kHz to 0.1 Hz after the 200th cycle. Cyclic voltammetry (CV) tests after 500 cycles were conducted on ZIVE MP1 in the potential range of 0.00–2.00 V at various scanning rates of 0.1, 0.2, 0.4, 0.6, and 1.0 mV s^{-1} to be utilized in the calculation of the Li^+ diffusion coefficient (D) of the as-prepared electrodes.

3. Results and discussion

Antimony nanoparticles were used as sacrificial templates, and they reacted with Fe^{3+} ions to develop $\text{Fe}_x\text{Sb}_y\text{O}_z$ hybrid oxide systems in the TEG medium via the galvanic replacement reaction. The difference

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