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Hierarchically structured carbon-coated SnO_2-Fe_3O_4 microparticles with enhanced lithium storage performance

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ABSTRACT

A facile and scalable strategy was developed to fabricate SnO_2-Fe_3O_4@C micrometer-sized particles as a good lithium-ion battery anode. The obtained materials were constructed by aggregated nanoclusters (100–200 nm) consisting of SnO_2-Fe_3O_4@C nanospheres (20 ~ 30 nm), in which SnO_2 and Fe_3O_4 nanoparticles (5 ~ 8 nm) were homogeneously embedded in a percolating carbonaceous network with an average thickness of about 3 nm. SnO_2-Fe_3O_4@C microparticles were synthesized by a one-pot hydrothermal process followed by annealing under Ar and subsequent chemical vapor transformation (CVT) under vacuum. The peculiar strategy allows to obtain hierarchical structure of micrometer-sized particles including nanospheres, nanoclusters and micro-scale particles, and the combination of SnO_2 and Fe_3O_4 could promote the synergistic effects to enhance the reversible capacity as well as the structural stability. Meanwhile, the carbon layer, homogeneously covering the nanoparticles does not only accommodate the volume change of active materials to maintain the structural integrity but also forms a conductive network throughout the whole micro-sized structure during charge/discharge processes. As a result, the electrode of SnO_2-Fe_3O_4@C microparticles exhibits good rate performance (1056 mAh g^{-1} at 0.1 C, 734 mAh g^{-1} at 0.2 C, 449 mAh g^{-1} at 0.5 C, 212 mAh g^{-1} at 1 C and 133 mAh g^{-1} at 2 C, 1 C = 1 A g^{-1}), high reversible capacity and good cycling stability (a high initial charge capacity of 1131.8 mAh g^{-1} was achieved and the capacity maintained 853.3 mAh g^{-1} after 50 cycles at 0.1 A g^{-1}).

1. Introduction

In order to develop next-generation lithium-ion batteries (LIBs) for application in electric vehicles and power grids, many critical issues must be addressed, such as energy density/power density and cycling stability [1–3]. However, current commercial graphite anodes with a low theoretical capacity of 372 mAh g^{-1} render a very limited energy output for LIBs, and alternative anode materials with higher reversible capacity and better rate capability together with long-term cycling stability are highly desired [4–6]. In this regard, Fe_3O_4, which not only has high theoretical storage capacity (926 mAh g^{-1} based on a conversion mechanism, $Fe_3O_4 + 8Li^+ + 8e^- \leftrightarrow 3Fe + 4Li_2O$), but also possesses the merits of low cost and eco-friendliness, has been intensively studied as a potential alternative anode material for high-performance LIBs [7–9]. However, the severe volume change of Fe_3O_4 during the charge/discharge processes would induce the pulverization of particle morphology and the loss of electrical connection of active materials from current collectors, thereby resulting in rapid capacity loss. Furthermore, the low electrical conductivity of pristine Fe_3O_4 usually further hastens the degradation process.

For the sake of addressing above issues, several strategies have been developed. The common method is to synthesize Fe_3O_4 nanostructures for reducing the Li^+ diffusion path and increasing the contact area between the electrode and the electrolyte, which improves the cycling stability and rate capability [10]. Nevertheless, its application in practical LIBs is still highly hampered by the large irreversible capacity (i.e., low columbic efficiency) and poor cycle life due to the unstable solid electrolyte interphase (SEI) films formed on their surface, which is attributable to the high

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surface-to-volume ratio and large surface free energy of the Fe_3O_4 nanostructures [10,11]. In addition, as a kind of conversion material, Fe_3O_4 may show large voltage hysteresis due to the electrode polarization during the charge/discharge processes, also resulting in comparably poor energy storage efficiency [12,13]. An interesting route is to elaborately design and construct nanocomposites of Fe_3O_4 in combination with other metal oxides (indicated with M_yO_x-Fe_3O_4) [14], such as Mn_3O_4-Fe_3O_4 [15], SnO_2-Fe_3O_4 [14,16] and TiO_2-Fe_3O_4 [17]. Owing to the synergistic effect between them, it is expected that these M_yO_x-Fe_3O_4 composites may possess good electrochemical properties [14]. Indeed, many studies validated that the synergistic effects led to a superior electrochemical properties (such as larger reversible capacity [18,19], better rate capability [14,20] and higher initial Coulombic efficiency [21–24]) over single phase materials. Despite the great progresses for the M_yO_x-Fe_3O_4 nanocomposites, the lithium storage performance still remains insufficient to fully realize their potential in LIBs due to the intrinsically poor electronic conductivity of metal oxides. In this regard, combining M_yO_x-Fe_3O_4 nanocomposites with carbon coating seems a good solution since carbon coatings not only act as a robust network to preserve good electronic conductivity of the overall electrode, but also function as a structural buffer to effectively accommodate the strain caused by the volume change of nanoparticles [14,22,23].

On the other hand, nanostructured electrodes may introduce new fundamental issues, including higher surface area, low tap density and generally poor electrical properties due to the higher interparticle resistance. The high surface area increases side reactions with the electrolyte and lowers the Coulombic efficiency. The low tap density leads to low volumetric capacity and a thick electrode at high mass loading, which makes it difficult to maintain favorable electrical and ionic pathways during cycling. Finally, electrical contact between the nanoparticles is easily altered or diminished due to the volume changes during cycling, thereby severely decreasing the cycle life of the electrode [25,26], recently, materials with micrometer-sized particles constructed by aggregated nano-sized particles were found to be able to overcome these shortcomings yet still maintain the advantages of nanomaterials [27–30]. All the resulting materials displayed much enhanced volumetric energy density compared with the corresponding nanoscale materials.

Herein, we demonstrate a novel and scalable method for synthesizing hierarchically structured SnO_2-Fe_3O_4@C microparticles for LIB anodes. The hierarchically structured SnO_2-Fe_3O_4@C microparticles are constructed by aggregated nanoclusters consisting of SnO_2-Fe_3O_4@C nanospheres (20–30 nm), in which SnO_2 and Fe_3O_4 nanoparticles ($5 \sim 8$ nm) are homogeneously embedded in a percolating carbonaceous network with an average thickness of about 3 nm. The synthetic process involves the preparation of Fe_2O_3@C microparticles through one-pot hydrothermal process using glucose and iron nitrate as precursors and poly(vinyl alcohol) (PVA) as a structure-directing agent during hydrothermal reaction, the conversion to Fe_3O_4@C microparticles by heat-treatment, and the generation of SnO_2-Fe_3O_4@C microparticles via chemical vapor transformation (CVT) process. To the best of our knowledge, the herein studied SnO_2-Fe_3O_4@C microparticles have not been reported and the peculiar strategy allows to obtain hierarchical structure of micrometer-sized particles including nanospheres, nanoclusters and micro-scale particles. In the constructed architecture, the combination of SnO_2 with Fe_3O_4 could promote the synergistic effects to enhance the reversible capacity as well as the structural stability. Meanwhile, the carbon layer, homogeneously covering the nanoparticles does not only accommodate the volume change of active materials to maintain the structural integrity but also forms a conductive network throughout the whole micro-sized structure during charge/discharge processes. As a result, the electrode based on SnO_2-Fe_3O_4@C microparticles exhibits good rate performance (1056 mAh g^{-1} at 0.1 C, 734 mAh g^{-1} at 0.2 C, 449 mAh g^{-1} at 0.5 C, 212 mAh g^{-1} at 1 C and 133 mAh g^{-1} at 2 C, 1 C = 1 A g^{-1}), high reversible capacity and good cycling stability (a high initial charge capacity of 1131.8 mAh g^{-1} was achieved and the capacity maintained 853.3 mAh g^{-1} after 50 cycles at 0.1 A g^{-1}).

2. Experimental

2.1. Synthesis of SnO_2-Fe_3O_4@C microparticles

SnO_2-Fe_3O_4@C microparticles were synthesized by a one-pot hydrothermal process followed by annealing under Ar and subsequent chemical vapor transformation (CVT) under vacuum. The chemicals, including polyvinyl alcohol (PVA), glucose ($C_6H_{12}O_6$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) and tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$), were purchased from Tianjin Chemical Reagent Company and used without further purification. In a typical synthesis, 0.1 g PVA was added to 80 ml deionized water and stirred in a water bath at 90 °C for 30 min to obtain PVA solution and $Fe(NO_3)_3{\cdot}9H_2O$ (6 mmol) was dissolved in 4 ml deionized water to obtain $Fe(NO_3)_3$ solution. Then the $Fe(NO_3)_3$ solution and $C_6H_{12}O_6$ (10 mmol) were added to the PVA solution and stirred for 10 min to homogenize the solution. The as-obtained mixed solution was transferred to a 50 ml Teflon-lined stainless-steel autoclave and heated at 190 °C for 9 h. Once cooled to room temperature naturally, the resulting solid was collected by centrifugation and washed thoroughly with deionized water for several times. After that, the acquired product was redispersed into a certain amount of deionized water, and freeze-dried to yield Fe_2O_3@C microparticles, which was further annealed at 500 °C for 2 h under a flowing Ar atmosphere to obtain Fe_3O_4@C microparticles. Eventually, the as-obtained Fe_3O_4@C microparticles (0.131 g) together with $SnCl_2{\cdot}2H_2O$ powders (1.816 g) were placed 1 cm apart in a tube furnace and heat-treated at 650 °C for 30 min under vacuum to form the SnO_2-Fe_3O_4@C microparticles.

2.2. Characterization techniques

The morphology and microstructure of the products were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) performed on a FEI Tecnai G^2 F20 TEM. Energy-dispersive X-ray spectroscopy (EDX) analyses were carried out with a spatially resolved EDX spectrometer attached to the TEM. Phase identification was performed by X-ray diffraction (XRD) using Cu K_α radiation at a wavelength of 1.5406 Å, and a step size of 0.02°. To validate the presence of carbon in the product, Raman spectra were recorded on a LabRAM HR Raman spectrometer using laser excitation at 514.5 nm from an argon ion laser source. The thermal properties were characterized by thermogravimetric analysis (TGA; TA instruments) under air at a flow rate of 100 ml min^{-1} over a temperature range of 40–1000 °C with a ramp rate of 10 °C min^{-1}. N_2 adsorption–desorption isotherms were measured with an autosorb iQ instrument (Quantachrome U.S.) at 77 K. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model.

2.3. Electrochemical measurements

To test the electrochemical performance, the active materials (SnO_2-Fe_3O_4@C microparticles, or Fe_3O_4@C microparticles), conductive agent (carbon black) and binder (polyvinylidene fluoride, PVDF) were added in turn with a weight ratio of 80:10:10 into a beaker. Subsequently, the slurry was obtained by adding