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Facile synthesis of monodisperse Co_3O_4 mesoporous microdisks as an anode material for lithium ion batteries

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ABSTRACT

The monodisperse Co_3O_4 mesoporous microdisks have been successfully prepared through a facile solvothermal synthesis method and subsequent heating treatment. The Co_3O_4 microdisks are polycrystalline, and have an average diameter of around 2 μm with an thickness of 300 nm. The specific surface area of Co_3O_4 mesoporous microdisks is about 108.9 $m^2 g^{-1}$ with a narrow pore size distribution centered at round 9.68 nm. The as-prepared Co_3O_4 mesoporous microdisks as anode material in lithium ion batteries exhibit a stable specific discharge–charge capacity of 765 and 749 mAh g^{-1} after 30 cycles at a current density of 100 mA g^{-1}. The good electrochemical properties could be attributed to the unique mesoporous structure of Co_3O_4 materials.

Introduction

Lithium-ion batteries (LIBs) have been considered as a promising candidate for energy conversion and storage technology in view of their significant advantages of high capacity, long cycling lifetime, no memory effect and environmental friendliness [1–7]. However, for large-scale applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs), much effort is still needed to design ideal electrode materials with specific morphology and composition to improve the properties of the LIBs.

Recently, anode electrodes made of transition-metal oxides have been widely investigated owing to their high theoretic capacity than that of commercially available electrodes such as graphite (theoretical capacity 378 mAh g^{-1}) [8,9]. Among the transition-metal oxides, Co_3O_4 has been extensively researched as a promising anode material for LIBs due to its high theoretical capacity (890 mAh g^{-1}), high tap density and stable chemical properties [10–12]. However, the poor cycling stability owing to the large volume changes during the repeated insertion and extraction of Li^+ limits its practical application in high-energy storage technology. In order to improve its cycle stability and rapid-rate capability, many researchers have focused on preparing various morphologies of Co_3O_4 anode materials for LIBs. Hollow spherical Co_3O_4 particles exhibit high reversible capacity of above 1000 mAh g^{-1} during up to 50 cycles and good rate capability [13]. Lu and coworkers [14] prepared different morphologies including nanoparticles, rod-like nanoclusters and macroporous platelets. Electrochemical results showed macroporous platelet-like Co_3O_4 morphology was the best suitable for reversible lithium storage properties. It displayed superior cycling performance and excellent high rate capacities (811 mAh g^{-1} at 1780 mA g^{-1} and 746 mAh g^{-1} at 4450 mA g^{-1}). Three-dimensional hierarchical pompon-like Co_3O_4 porous spheres showed higher specific capacity and better cycle performance than those of Co_3O_4 nanoparticles and nanowires [15]. Liu and coworkers reported [16] the synthesis of unusual single-crystal Co_3O_4 nanocages with highly exposed {110} reactive facets via a one-step solution method. When tested as anode materials in lithium-ion batteries, these Co_3O_4 nanocages deliver a high reversible lithium storage capacity of 864 mAh g^{-1} at 0.2 C over 50 cycles and exhibit an excellent rate capability. Chen and workers [17] developed a facile method to synthesize large Co_3O_4 nanocubes, hexagonal naodiscs and nanoflowers. These three Co_3O_4 samples were investigated the comparative lithium storage properties. The electrochemical measurements show that the nanoflower sample exhibits the best performance with quite reversible capacities (649 mAh g^{-1} after 100 cycles). Therefore, Study of the structural effect on magnetic properties of these Co_3O_4 nanostructured materials should also be interesting. However, to the best of our knowledge, for Co_3O_4, its mesoporous microdisk architecture applied as anode material for LIBs has not been reported so far.

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Herein, we have successfully synthesized unique and uniform Co_3O_4 mesoporous microdisks through a facile template-free solvothermal method in a mixed solution of isopropyl alcohol (IPA) and water at relatively low temperature, followed by a post calcinating treatment. The experimental process is illustrated in Fig. 1. In step 1 (S1), monodisperse $Co_2(OH)_2CO_3$ microdisks are prepared by a facile solvothermal process without any template, surfactant or catalyst. In step 2 (S2), the $Co_2(OH)_2CO_3$ microdisks are calcined under air atmosphere at 300 °C to obtain the mesoporous Co_3O_4 microdisks by the release of CO_2 and H_2O gas. When tested as anode materials for LIBs, as shown in the step 3 (S3), the as-prepared Co_3O_4 electrode composed of numerous pores will reduce Li^+ diffusion distance, which can enhance the electrochemical behaviors. The specific surface area of Co_3O_4 mesoporous microdisks is about 108.9 $m^2\,g^{-1}$ with a narrow pore size distribution centered at round 9.68 nm. They exhibit a stable specific discharge-charge capacity of 764.5 and 748.6 mAh g^{-1} after 30 cycles at a current density of 100 mA g^{-1}.

Experimental

Material synthesis

All chemical reagents were of analytical grade and used as received without any further purification. In a typical synthesis procedure, 10 mmol $CoCl_2\,6H_2O$ was dissolved in 85 ml of isopropyl alcohol (IPA). The mixture was stirred vigorously for 20 min to form solution A. 18 mmol of Na_2CO_3 was dissolved in 35 ml of distilled water to form solution B. Solution B was poured into the solution A sequentially under stirring. Then the mixture was sealed in a Teflon-lined stainless-steel autoclave. The autoclave was put into an oven and kept at 80 °C for 5 hours. The light pink precipitates were collected by centrifugation, washed by deionized water and ethanol for three times, and dried at 60 °C in the vacuum drying oven. In order to obtain micro-disk Co_3O_4 sample, the precursor was annealed at 300 °C for 2 hours in air (1 °C min^{-1}) with an electric furnace.

Material characterization

Crystal structure of the as-prepared product was characterized by X-ray diffraction (XRD) using D8 ADVANCE (3 KW) with Cu K radiation. The morphology was investigated by the field emission scanning electron microscope (FESEM, JSM-7001F) with energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (FEI Tecnai G^2 F30). Raman measurement was carried out on a Renishaw RM2000Confocal Raman Spectrometer with an excitation line of 514 nm. The element analysis was measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 instrument). Nitrogen adsorption and desorption isotherms were performed at 77 K on a Quantachrome NOVA4200E (USA) volumetric adsorption system.

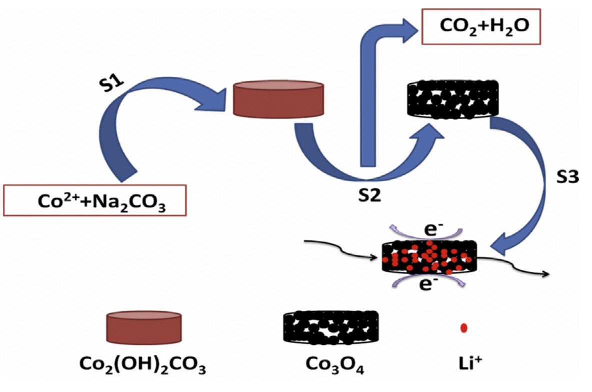

Fig. 1. Schematic illustration of the formation process of Co_3O_4 mesoporous microdisks and their presented electrochemical property in lithium-ion storage.

Electrochemical measurement

The electrochemical performance of as-prepared Co_3O_4 sample was evaluated using the CR2032-type coin cells. As-prepared micro-disk Co_3O_4 as active material was mixed with acetylene black as conductive agent and polytetrafluoroethylene as binder at a weight ratio of 70:20:10 to fabricate anode. The anode was dried in a vacuum at 120 °C for 12 hours. The CR2032-type coin cells were assembled in an argon filled glove-box with lithium foil as counter electrode, Celgard 2500 film as the separator. The electrolyte is 1 mol L^{-1} solution of $LiPF_6$ dissolved in a mixture of ethylene carbonate/dimethyl carbonate/diethylene carbonate (EC/DMC/DEC) with volume ratio of 1:1:1. The loading of active material in a typical electrode disk contained 8–10 mg cm^{-2}, and the thickness of the electrode disk was about 10 μm. The cyclic voltammogram (CV) was performed on an electrochemical workstation (CHI 660E) at a scan rate of 0.1 mV s^{-1} with potential range from 0.01–3.00 V (vs. Li^+/Li). The discharge/charge tests were conducted on LAND batteries test system (Wuhan, China) at various densities of 100–800 mA/g with a potential range of 0.01–3.0 V vs. Li^+/Li at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage of 5 mV over the frequency range was from 10^{-2}–10^5 Hz (ZAHNER Im6e)

Results and discussion

Structural characterization of monodisperse Co_3O_4 mesoporous microdisks

The crystal structure and phase purity of the as-prepared sample are characterized using XRD. Fig. 2a (Red) shows the typical XRD pattern of the precursor prepared by solvothermal reaction. By compared the peak positions with the standard PDF files, it is clearly seen that the precursor is composed of $Co_2(OH)_2CO_3$ (JCPDS no 48-0083) [18]. Fig. 2a (Black) presents the as-prepared Co_3O_4 mesoporous microdisks after calcinations 300 °C for 2 h in air. All diffraction peaks are good agreement with that of cubic spinel Co_3O_4 (JCPDS no 42-1467) [10,19,20]. No impurities have been observed, indicating the formation of pure cobalt oxides.

TG–DTG was conducted for the as-prepared $Co_2(OH)_2CO_3$ precursor in air atmosphere to examine the conversion process during calcinations. As shown in Fig. 2b, the sample weight decreases slowly between 30 and 200 °C. This is attributed to the elimination of absorbed water in the sample. An obvious weight loss is observed between 200 and 284 °C on the TG curve, suggesting that thermal decomposition takes place, leading to the formation of Co_3O_4 in this range [21]. Therefore, a temperature of 300 °C is selected as the transformation temperature for preparation of Co_3O_4 phase.

Moreover, the chemical composition of the products can be further provided by XPS measurements, as shown in Fig. 2c, the Co 2p XPS spectrum displays two major peaks at 779.2 and 794.4 eV, corresponding to Co $2P_{3/2}$ and Co $2P_{1/2}$, respectively, with a spin-orbit splitting of 15.2 eV. The absence of shake-up satellite peaks with binding energies at 789.2 and 804.2 eV further suggests the formation of the Co_3O_4 phase [22,23]. The deconvoluted O 1s spectrum in Fig. 2d shows two peaks with binding energies at 530.1 and 531.4 eV, which are attributed to the lattice oxygen species in the spinel Co_3O_4 and the oxygen in the hydroxide ions