



Enhanced electrochemical performance of flower-like Co_3O_4 as an anode material for high performance lithium-ion batteries



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ARTICLE INFO

Article history:

Received 26 June 2014

Received in revised form 4 September 2014

Accepted 11 September 2014

Available online 16 September 2014

Keywords:

Cobalt Oxide

flower-like

nanorods

Specific capacity

chemical co-precipitation

ABSTRACT

A facile urea-assisted template-free, surfactant-less chemical co-precipitation method was used to obtain a flower-like cobalt oxide sample followed by annealing at various temperatures of 400, 500, and 600 °C for 2 h. The obtained flower-like morphology was assembled by nanorods, and the nanorods were comprised of interconnected particles with a porous structure. The changes in the surface area of the obtained flower-like Co_3O_4 samples were systematically examined at various temperatures and their impact on the electrochemical performances was observed. Electrochemical investigation showed that the flower-like Co_3O_4 samples obtained at 500 °C, showed excellent cycling stability (1536.9 mA h g^{-1} at 0.1 C up to 50 cycles and 1226.9 mA h g^{-1} at 0.5 C up to 350 cycles) and superior rate capability (845 mA h g^{-1} at 10 C). It is believed that the porous nature of the unique structure facilitates the penetration of the electrolyte at the electrode/electrolyte interface and provides a large space for strain buffering, which ultimately allows the present sample to achieve high rate performances.

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1. Introduction

Since the last decade, significant interest has been paid to the development of energy storage devices. Energy storage devices play an important role in the portable electronic devices. Nowadays, Lithium ion batteries (LIBs) are the main source of energy for portable electronic devices such as notebook-style personal computers, smart phones, plug-in hybrid vehicles, and electric vehicles [1]. Nevertheless, the energy density and safety of LIBs is still a challenge for most applications. In short, the energy density, cycle life, and safety further need to increase for successful application in the automobile industry. The conventional graphite anode material have a low theoretical capacity (370 mAh g^{-1}), which limits its further application in next generation high power lithium ion batteries. To improve the electrochemical performance of LIBs, intense efforts have been made to find new anode material that will increase the storage capacity of lithium ions. Recently, transition metal oxides (TMOs) have attracted much attention as anode materials for LIBs due to their high theoretical capacity ($\sim 700 \text{mAh g}^{-1}$), long cycle life, and high rate performances [2–7]. Among various transition metal oxides, cobalt oxide (Co_3O_4) has been intensively

investigated as a promising anode material for LIBs owing to its high specific capacity, good cycling stability, high rate performance, and low cost [8–11]. More importantly, Co_3O_4 can store more than eight lithium atoms per formula unit according to the redox reaction ($\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}$). The theoretical capacity of Co_3O_4 as per the proposed reaction can be calculated to be 890 mA h g^{-1} , which is nearly two times higher than that delivered by conventional carbonaceous graphite anode [2,12]. However, similarly to other metal oxide anode materials, Co_3O_4 also suffers from poor capacity retention and low rate capability, because of the volume change and serious aggregation during discharge/charge cycling. However, the limitations of TMO materials could be possibly overcome by making a unique structure with capabilities to sustain structural disintegration during cycling and promote lithium ion storage. Furthermore, it is well-known that the lithium ion storage properties can be enhanced through tailoring the morphology and pore size distributions [5]. Different proposals based on the tailored morphology, the formation of nanocomposites with conductive additives, and the nano-sized Co_3O_4 electrode materials have been attempted to address this issue [13]. In addition, various Co_3O_4 materials including nanotubes [10,14], nanorods [15], nano-needles [16–17], nanospheres [18], platelets [19], and nanowires [20–21] have been synthesized to reduce the diffusion length for both electrons (e^-) and Li^+ ions, and to partially accommodate the volume variation during the Li^+ insertion/extraction, which can improve the capacity retention and rate capability.

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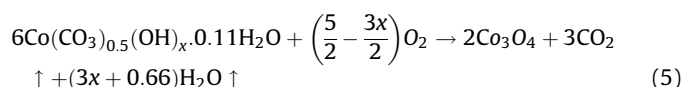
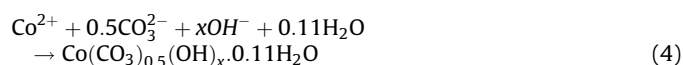
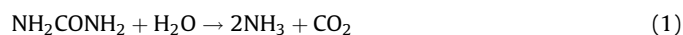
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The present study illustrates the synthesis of flower-like porous structured Co_3O_4 by a facile chemical co-precipitation method followed by annealing at various temperatures. We have clearly investigated the effect of annealing temperatures on the morphology and electrochemical performances when Co_3O_4 is used as an anode material for LIBs. As a potential anode material, the optimized porous flower-like Co_3O_4 obtained at 500°C exhibits high reversible capacity, stable cyclability, and excellent rate capability. The porous nature of the unique structure facilitates the penetration of the electrolyte at the electrode/electrolyte interface and provides a large space for strain buffering, which ultimately allows the present sample to achieve high performances.

2. Experimental method

2.1. Synthesis of flower-like Co_3O_4

In a typical synthesis, a stoichiometric amount of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99.5% Junsei, Japan) and urea (NH_2CONH_2 , 99% Aldrich) were dissolved in deionized water (DI) under vigorous stirring for 30 min. The prepared aqueous solution was then kept at 90°C for 10 h in an oil bath and the pH was maintained. The precipitation started when a constant pH was maintained. During the precipitation, a heterogeneous reaction occurred leading to the formation of cobalt hydroxy carbonate as an intermediate phase. The obtained precipitate was washed with DI water several times to remove the residual organic impurities, and collected by centrifugation at 3000 rpm for 10 min. The obtained precipitates were then dried overnight in a vacuum oven at 100°C . Further annealing of the obtained precipitate at various temperatures of 400, 500 and 600°C for 2 h in air produced the Co_3O_4 nano-materials, which were assigned as S-400, S-500, and S-600, respectively. The chemical reactions involved in the formation of the Co_3O_4 phase can be described in the following steps [22–24]:



2.2. Material Characterization

Thermo-gravimetric analysis (TG) was carried out using a thermogravimetric analyzer (Perkin Elmer TGA7) at a scan rate of 10°Cmin^{-1} in an air atmosphere. The phase structure and morphology of the annealed samples were characterized by X-ray diffraction (XRD, Rigaku DIII vitima with $\text{Cu K}\alpha$ radiation), and field-emission scanning electron microscopy (FE-SEM, S-4700Hitachi), high-resolution transmission electron microscopy (HR-TEM, Philips Tecnai F20 at 200 kV). The X-ray photoelectron spectrum (XPS) was measured using an ESCALAB-MKII spectrometer (UK) with $\text{Al K}\alpha$ radiation (1486.6 eV) as the X-ray source for excitation, and the binding energies (BEs) were evaluated using C1s spectrum (BE = 284.6 eV) as the reference with the accuracy

of ± 0.1 eV. The surface areas of the samples were determined by nitrogen adsorption and desorption isotherms using a Brunauer–Emmett–Teller instrument (BET, Micromeritics ASAP2010 Instrument Co., Norcross, GA, USA).

2.3. Electrochemical tests

The electrochemical performances of the obtained Co_3O_4 samples were tested by using the coin type half cells with lithium metal as the counter electrode. For the preparation of electrodes, the annealed samples were first uniformly mixed with super-P and PVDF at a weight ratio of 70:20:10 in a N-methyl-2-pyrrolidone solvent to form slurry. The obtained slurry was pasted onto a pure copper foil as a current collector followed by drying in a vacuum at 100°C for 10 h. The electrolyte was 1 M LiPF_6 dissolved in a 1:1 (volume ratio) mixture of ethylene carbonate and dimethyl carbonate. The cells were assembled in an argon-filled glove-box. The cells were galvanostatically cycled between 0.005 ~ 3.0 V vs. Li/Li^+ at different C-rates using a Won-A-Tech WMPG-1000 battery cycler. The cyclic voltammogram (CV) was obtained at a scan rate of 0.1 mV s^{-1} in the voltage range of 0 ~ 3.0 V (vs. Li/Li^+) using the Won-A-Tech potentiostat/Galvanostat instrument. The AC impedance measurements of the assembled half-cells were carried out after 50 cycles using the ZIVE SP2 instrument at a frequency range of 1 Hz ~ 1 MHz at voltage amplitude of 10 mV.

3. Results and Discussion

3.1. Crystal structure and morphology

The as-prepared sample obtained at 90°C was used for the TG analysis to study the thermal decomposition process. Fig. 1 shows the TG curve of the as-prepared powder. The total 28.27% weight loss was observed during the measurement. The weight loss upto $\sim 360^\circ\text{C}$ was assumed to be due to the loss of residual water, burnout of organic species involved in the precursor powders, and the decomposition of the intermediate phase into Co_3O_4 . However, above 360°C , no obvious weight loss appears, thereby indicating the completion of the entire reaction. Therefore, to optimize the annealing temperature and high crystallinity for the flower-like pure Co_3O_4 sample, various temperatures of 400, 500, and 600°C were identified.

Fig. 2 shows the XRD patterns of the as prepared sample obtained at 90°C and the annealed samples of S-400, S-500, and S-600. All the diffraction peaks of the as prepared sample obtained at 90°C , are well indexed with an intermediate phase of cobalt hydroxy carbonate (JCPDS No.48-0083). Furthermore, the XRD

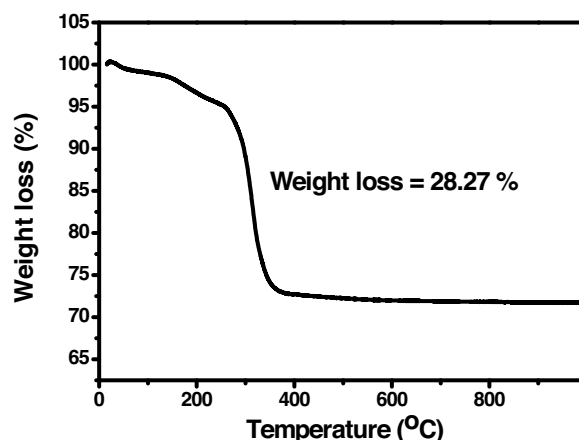


Fig.1. TG curve of the as prepared sample obtained at 90°C .

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