Hierarchical Co_3O_4 Nanoparticles Embedded in a Carbon Matrix for Lithium-Ion Battery Anode Materials

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ABSTRACT

A Co_3O_4-C nanocomposite has been synthesized by a one-step hydrothermal method free of any template with an annealing process. The composite exhibits a flower-like, hollow, and porous skeleton with a large specific surface area of 272.3 m^2g^{-1}. The scanning electron microscope (SEM) and transmission electron microscope (TEM) images reveal the hybrid nanostructure comprises ring-like Co_3O_4 nanocrystals of 20 nm in diameter homogeneously embedded in the carbon matrix. Such integrated electrodes exhibit an ultrahigh specific capacity and excellent cycling stability even at a high charge/discharge current density. Cycle exceeds 400 times in half cells at a 5 C (5 Ag^{-1}) rate while retaining about 1000 $mAhg^{-1}$ reversible capacities (where a 1 C rate represents a one-hour complete charge or discharge). This study not only provides a simple synthesis method for lithium ion batteries, but also helps in designing novel and high performance electrode materials.

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1. Introduction

Global energy and environment issues make sustainable next-generation energy storage systems more important. Rechargeable lithium-ion batteries(LIBs) have been considered as the most promising energy storage system for the advantages such as long cycle life, high reversible capacity, low self-discharge, high operating voltage and no "memory effect" [1,2]. LIBs have been widely applied in portable electronic devices [3]. The main challenge of the field is to make the electric vehicle commercially viable [4,5]. This requires high energy and power densities without compromise in safety [6,7]. Carbonaceous materials are currently predominant anode active materials in commercial rechargeable lithium-ion batteries for their low cost, low toxicity, good conductivity and reversibility [8]. But the theoretical capacity is limited and far from meeting the growing demand of energy storage system.

Transition metal oxide such as Co_3O_4 has attracted increasing attention with a high theoretic capacity about three times as that of graphite [9,10]. Various Co_3O_4 nanostructures such as nanowires, nanorods, nanotubes, nanoflowers, and nanocages arrays have been fabricated to improve the lithium battery performance [11–15]. It is well known that the morphology, specific surface area, crystallinity and structure stability of nanomaterials all have significant effects on the charge/discharge performance [10]. Small particles would more easily accommadate the structural changes resulted by Li-ion insertion and extraction during cycling process. The nanomaterials have large specific surface area and small depth for Li-ion diffusion, which favors the interaction between the electrodes and Li-ions [16,17]. In nanoparticles, the charge accommodation occurs largely at or very near the surface. The small demensions not only reduce the need for diffusion of Li-ion in the solid phase, but also alleviate the volumetric changes and lattice stresses caused by repeated Li insertion and extraction [18,19]. Therefore nanoparticles can dramatically enhance capacity retention ability. However, they tend to aggregate during Li-ion insertion/extraction,consequently resulting in a large irreversible capacity loss and poor cycling stability [20,21]. This issue can be circumvented by coating the nanomaterials with a thin layer of carbon [22,23]. The carbon can bring the required conductivity to individual grains and buffer the strain associated with lithium insertion/extraction reactions [24]. Recently, a few reports have ever been made on the synthesis of Co_3O_4/C nanocomposite for lithium ion battery applications [25,26]. In addition, designing hollow and porous structures is another strategy to improve the electrochemical performance of nanomaterials [7,27]. The void space in hollow or porous structure can accommodate volume

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change during Li$^+$ insertion/extraction and is able to alleviate pulverization and aggregation of electrode materials, hence improving cycle performance [28]. Template synthesis can result in well-controlled hollow structures with porosity and interconnectivity [29,30]. For example, virus-templated Co$_3$O$_4$ nanowires have been demonstrated as an improved anode for lithium ion batteries [31]. The template itself is costly and the controlled removal of the template by either thermal or chemical means is hard and complicated [32]. Hydrothermal synthesis is an easy and low-cost approach for producing many inorganic materials with homogeneous micro- or nanostructures [33].

In this study, we reported a one-step hydrothermal method free of any template for synthesizing Co$_3$O$_4$-C nanocomposite. Gluconate, which has been used as a source for carbon materials [34], undergoes successive reactions under hydrothermal treatment, that is, polymerization and carbonization. This structure supplies extra accessible space for lithium ions insertion/extraction, maintains morphological stability and sufficient conductivity for solid electronic transfer. The carbon skeleton can enhance the electron conductivity and accommodate the volume change during the Li ion insertion/extraction. In addition, the electrochemical performance of the nanocomposite was evaluated. The specific capacity and rate capability are significantly enhanced, indicating a promising candidate for lithium batteries.

2. Experimental Details

2.1. Materials synthesis

We choose organic metal salts Co(C$_6$H$_{11}$O$_7$)$_2$ as the precursor. 1 mmol cobalt (II) gluconate [Co(C$_6$H$_{11}$O$_7$)$_2$] was dissolved in 40 mL H$_2$O to form a clear solution under stirring for 30 min at room temperature. Afterward, the pH was adjusted to ~4 by adding commercial HCl solution. Finally the mixture was transferred into a 50 mL Teflon-lined autoclave, then heated to 200 °C at rate of 5 °C• min^{-1}, and maintained at this temperature for 20 h. The reactor was cooled to room temperature naturally. The resultant product was collected and washed several times with alcohol and deionized water, and then dried at 80 °C in air. The as-prepared precursor was finally calcined at 700 °C in an argon atmosphere for 3 h to obtain Co–Carbon nanocomposite and then calcined at 250 °C in air for 3 h to obtain Co$_3$O$_4$-Carbon nanocomposite.

2.2. Physicochemical Characterization

The phase purity of the composite was characterized by XRD operated at 30 kV and 30 mA with Cu Kα radiation scanning at 5 °C•min^{-1}. Raman spectroscopic analysis was performed with a Renishaw In-Via System utilizing a 514.5 nm incident radiation. The morphologies and microstructures of the composite were characterized by SEM (Quanta 400F) and TEM (FEI Tecnai G2 Spirit, FEI Tecnai G2 F30) and energy dispersive spectrum (EDS) mounted on SEM (Quanta 400F). Thermogravimetric analysis (TGA) was recorded from room temperature to 800 °C with a ramp rate of 10 °C•min^{-1} under ambient atmosphere.

2.3. Electrochemical characterization

In order to evaluate the electrochemical performance of the cobalt oxide-based nanocomposite, Co$_3$O$_4$-carbon nanocomposite (70 wt%), conducting additive (20 wt %, Super-P carbon black), sodium alginate (10 wt %) was mixed with deionized water by grinding in an agate mortar. The slurry mixture were pasted on a copper foil current collector by an automatic thick film coater (AFA-I) and dried at 90 °C for 2 h. After that, the foil is pressed by an electromotive roller (MR-100A) and tailored to appropriate size by a coin-type cell microtome (T-06).

Electrochemical test cells were assembled in an argon-filled glovebox using the coated copper foil as the working electrode, a lithium metal foil as the counter/reference electrode, and 1 M solution of LiPF$_6$ in a 50:50 w/w mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. Cyclic voltammogram of the composite electrodes were scanned at 0.2 mVs^{-1} in a voltage window of 0-3.36 V on an Ivium electrochemical workstation. Electrochemical impedance spectroscopy(EIS) measurements of the electrodes were also carried out using the same potentiostat at frequencies from 100 kHz to 0.01 Hz. For cycling and rate performance, the electrodes were galvanostatically charged and discharged in a voltage cutoff of 0.005-3 V at various rates on a multichannel Neware battery testing system.

3. Results and discussion

Fig. 1a shows the XRD patterns of the intermediate and the final product obtained by annealing the intermediate in Ar atmosphere for 3 h. The former corresponds to Co(CO$_3$)$_{0.5}$ (OH) 0.11H$_2$O (JCPDS No.48-0084) [35]. After thermal treatments, the type of the crystal is changed and all the reflection peaks of final product agreed well with literature pattern for Co$_3$O$_4$ (JCPDS No.43-1003). The diffraction peaks at 19°, 31.3°,36.8°, 44.8°, 59.4°, 65.2°(2θ) correspond to (111),(220), (311), (400), (511), (440) crystal planes of Co$_3$O$_4$ respectively. No significant impurities or other phases were observed, indicating that the total conversion from the precursor to Co$_3$O$_4$.

The Raman spectra of the Co$_3$O$_4$-C nanocomposites (Fig. 1b) further confirmed the co-existence of carbon and Co$_3$O$_4$. Five Raman peaks at 191, 473, 514, 613, 678, 1342 and 1591 cm^{-1} were noticed in the spectra at ambient conditions. The peaks at 1342 and 1591 cm^{-1} can be attributed to D band and G band of carbon consistent well with previous reports [36,37]. The D band is associated with disordered carbon, while the G band is the result of the first-order scattering of the E$_{2g}$ mode of sp^2 carbon domains, indicating that the carbon is partial graphitized. Other peaks are in good correspondence with bands of Co$_3$O$_4$ [38,39].The band at 671 cm^{-1} is characteristic of the octahedral sites (CoO$_6$), which is assigned to the A$_{1g}$ species, in the O$_7$ ^{h} spectroscopic symmetry. The Raman band located at 470 cm^{-1} has the E$_g$ symmetry, whereas the band at 191, 514, 613 cm^{-1} corresponds to the tetrahedral sites (CoO$_4$), which is attributed to the F$_{2g}$ symmetry.

The morphology and size of Co$_3$O$_4$-C were examined by SEM. Fig. 2a and 2b show the SEM images of precursors. The precursors are microflower-like and the surface of precursors consist of tiny nanowires as building blocks. After being annealed, precursors release volatile gas such as H$_2$O and CO$_2$ .But the morphology and size are rarely changed, as shown in the fig. 2c and 2d. Such unique structure provides an important morphological basic helping to enlarge the contact area, to make the best of the electroactive material Co$_3$O$_4$-C and to accelerate the transfer of ion and electron. EDS was used to determine the chemical composition of the final products (Fig. 2c(Inset)). Four major peaks correspond to the elements C, O, Co and Si, while Si derives from the substrate.

The TEM images of Co$_3$O$_4$-C conform the hollow structure. In fig. 3a, the pale inside was encapsulated by an obvious dark shell. The hollow structure is composed of Co$_3$O$_4$ nanoparticles with a size of 10~20 nm homogeneously embedded in the carbon matrix (fig. 3b). The Co$_3$O$_4$ nanoparticles are ringlike with micropores inside. EDS mapping was used to examine the distribution of C, Co, and O elements in the final product. The figs. 3b(Inset) correspond to C K-edge, Co L-edge, and O K-edge, respectively. It can be seen that Co$_3$O$_4$ nanoparticles are homogeneously embedded