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Ultrathin mesoporous $ZnCo_2O_4$ nanosheets as anode materials for high-performance lithium-ion batteries

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ABSTRACT

Transition-metal oxides have been widely explored as the anode materials for lithium-ion batteries (LIBs) because of its low cost and high energy/power density. However, the electrode pulverization and capacity fading during cycling lead to poor cycling performance. Herein, ultrathin $ZnCo_2O_4$ nanosheets with desired mesoporosity and high surface area are prepared by a facile hydrothermal approach. Such $ZnCo_2O_4$ nanostructures show excellent lithium storage performance as anode materials for LIBs. At a current density of 1 A g^{-1}, the ultrathin $ZnCo_2O_4$ nanosheets present an initial specific capacity of 1251 mAh g^{-1} and the specific capacity remains at ~810 mAh g^{-1} even after 200 discharge–charge cycles.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the dominant power source for consumer electronics and are being urgently needed in high-energy applications due to their high energy density, long cycle life, and environmental benignity [1]. Therefore, numerous efforts have been devoted to explore new remarkable electrode materials with low cost and high energy density. Transition-metal oxides (TMOs) have attracted widespread attention as promising lithium-storage anode materials for LIBs which possess higher specific capacities and stronger cycling stability than commercial graphite [2]. Among various TMOs, spinel structured ternary oxides $ZnCo_2O_4$ have generated increasing interest because of its high theoretical capacitance, strong cycling stability, low cost and high abundance. Compared with ZnO or cobalt oxides (CoO, Co_2O_3 and Co_3O_4), the ternary oxide $ZnCo_2O_4$ shows superior electronic conductivity and higher electrochemical activity [3]. Furthermore, $ZnCo_2O_4$ has the capability to reserve Li^+ through two types of reaction. This can not only produce Li_2O and nanocrystalline metal nanoparticles by conversion reaction but also form alloyed metal phase (LiZn) by alloying-de-alloying reaction [4] that lead to high theoretical capacity. However, limitations including poor rate capability, electrode pulverization and capacity fading during the extended cycling are still remaining and prevent it from commercialization [5].

It is proposed that the fabrication of nanostructured $ZnCo_2O_4$ with high surface area and fast electron/ion transport pathways can enhance its electrochemical performance [6]. Two-dimension (2D) nanostructures can promote the effective interaction between electrode/electrolyte and shorten the diffusion distance of electron/ion [7]. 2D ultrathin nanosheets-based anode materials exhibit improved kinetics because of the enhanced electrical conductivity and large number of surface atoms [8]. The mesoporous structure with nano-sized regions or domains display high capacity, due to acceleration of electrochemical reaction and penetration of the electrolyte. In addition, the free space can prevent the agglomeration and minimize the volume expansion of anode materials during lithium ion insertion/extraction [9]. The 2D ultrathin nanosheets with desired mesoporosity show prominent cycle performance and strong stability because the product has large surface area for high Li^+ flux across, rich lithium-storage sites and accelerated electrochemical reaction [10,11]. Therefore, it is necessary to prepare ultrathin mesoporous $ZnCo_2O_4$ nanosheets to further promote the performances of LIBs.

In this paper, we report the synthesis of ultrathin $ZnCo_2O_4$ nanosheets with desired mesoporosity via a facile hydrothermal

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method combined with annealing treatment. The ultrathin mesoporous $ZnCo_2O_4$ nanosheets can not only provide rich lithium-storage sites and fast de/lithiation reaction but also accommodate structural change during discharge/charge process. Benefiting from this nanostructure, the $ZnCo_2O_4$ anode exhibits high reversible capacity, superior cycle performance and high rate capability.

2. Experimental

2.1. Materials preparation

0.66 g $Zn(CH_3COO)_2 \cdot 2H_2O$, 1.5 g $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.3 g $NaHCO_3$ are dissolved in 10 mL deionized water under vigorous stirring, and then, added 10 mL ethanol amine to the mixture under stirring for 1 h at room temperature. Then the mixture is transferred into a 30 mL Teflon-sealed autoclave and maintained at 180 °C for 24 h. After the hydrothermally-treated solution is cooled to room temperature, the obtained products are centrifuged and washed with deionized water and ethanol at least 5 times separately, dried at 60 °C overnight and annealed at 400 °C for 120 min in air, resulting in the final product.

2.2. Materials characterizations

The obtained samples are characterized by X-ray diffraction (XRD, Rigaku D/Max III diffractometer with Cu Kα-radiation, $\lambda = 1.5418$ Å), scanning electron microscopy (SEM, Nova Nano SEM 230), transmission electron microscopy (TEM, Tecnai G^2F20, FEI), high-resolution TEM (HRTEM, Tecnai G^2F20, FEI), BET analysis (ASAP 2010).

2.3. Electrochemical measurements

For electrochemical tests, the working electrodes are prepared with active materials, acetylene black (AB), and Polyvinylidene Fluoride (PVDF) at the weight ratio of 75: 15: 10. The average weight of the active materials is ~1.5 mg. In the test cells, the lithium serves as the counter and reference electrode, Celgard 2300 serves as separator. The electrolyte is 1 M $LiPF_6$ dissolved in a 1: 1: 1 mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC). The cells are assembled in a glove box filled with high-purity argon. The galvanostatic charge and discharge tests are performed with a battery tester LAND-CT2001A in the voltage range of 0.001–3.0 V at room temperature. Electrochemical impedance spectroscopy (EIS) was taken by using an IM6e electrochemical workstation at 25 °C with the frequency range from 10 kHz to 100 mHz and an AC signal of 5 mV in amplitude as the perturbation. Cyclic voltammetry (CV) tests were performed at 5 mV s^{-1} between 0.001 and 3.0 V. The specific capacity is calculated according to the corresponding total weight of active materials in each electrode.

3. Results and discussion

We firstly prepared ultrathin ZnCo-precursors nanosheets (Fig. 1) through a facile hydrothermal method (see the Supporting Information for details), and then annealed the ZnCo-precursors at 400 °C in air to obtain 2D ultrathin nanosheets with desirable mesoporosity. As shown from the SEM images in Fig. 1, the ZnCo-precursor has a fairly uniform micro-structure consisted of wrinkled nanosheets (Fig. 1A). Higher magnification (Fig. 1B) shows that the precursor is composed of nanosheets with a micron-sized planar area and ultrathin thickness. After annealing, the wrinkled morphology of the precursor was preserved in the final $ZnCo_2O_4$ samples (Fig. 2A) but the smooth surface of the nanosheets became rougher. As a result of releasing H_2O and CO_2 from the precursor during the heating process (Fig. 2B) the $ZnCo_2O_4$ nanosheets are composed of nanoparticles and numerous pores. XRD patterns of the $ZnCo_2O_4$ nanosheets are shown in Fig. 2C. All diffraction peaks of the as-prepared sample could be assigned to cubic spinel $ZnCo_2O_4$ (JCPDS Card No. 23–1390; Space group: Fd^3m, $a = b = c = 8.0946$ Å) and there is no other impurity peak. The exact thickness of $ZnCo_2O_4$ nanosheets was obtained from employing atomic force microscopy characterization (AFM, Fig. 3). As it can be seen, the thickness of $ZnCo_2O_4$ nanosheets ranges from ~2.4 to ~4.3 nm, which indicates that the nanosheets consist of about 3–5 unit cells (a single $ZnCo_2O_4$ unit cell along c direction is ~0.81 nm). In this spinel structure, Zn^{2+} occupies the tetrahedral sites and Co^{3+} occupies the octahedral sites [12].

The morphology and porous structure of ZCO nanosheets are further investigated by TEM images. Fig. 4A provides a representative TEM image for the ZCO nanosheets, revealing well-defined nanosheet morphology, which possess folded morphology. Fig. 4B and C clearly show ZCO nanosheets own numerous pores and ultrathin thickness, and the pores are constituted of nanoparticles. The HRTEM image (Fig. 4D) shows two sets of lattice fringes with spacings of 0.29 and 0.25 nm, corresponding to the (220) plane and (311) plane of $ZnCo_2O_4$ phase, respectively, which are consistent with the XRD results. And the TEM and HRTEM images further confirm the porous structure and highly crystalline of the ZCO nanosheets.

The N_2 adsorption–desorption measurement (Fig. 5) are carried out investigating the porous structure and specific surface area of the as-prepared ZCO nanosheets and the electrode materials. As

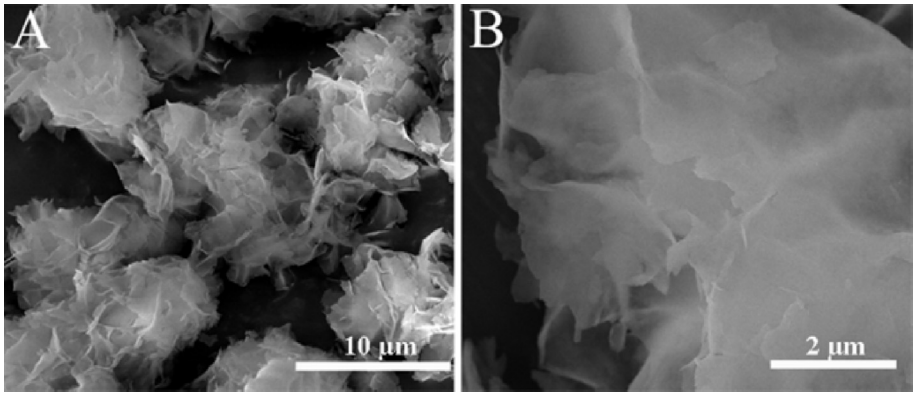

Fig. 1. SEM images of the as-prepared ZnCo-precursors.