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Template-free synthesis of mesoporous nanoring-like Zn-Co mixed oxides with high lithium storage performance

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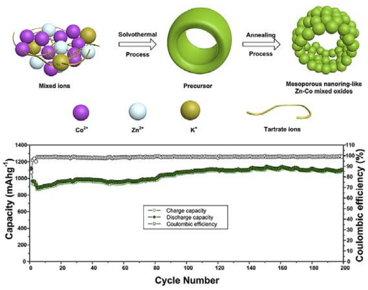
HIGHLIGHTS

- Mesoporous nanoring-like Zn-Co mixed oxides are synthesized via a simple method.
- Potassium sodium tartrate is added as a special complexing agent.
- The mesoporous ringent nanostructure is advantageous in improving cell performance.
- The nanoring-like Zn-Co mixed oxides show excellent cycling stability and rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous nanoring-like Zn-Co mixed oxides are synthesized via a simple template-free solvothermal method with a subsequent annealing process. The ring-like nanostructures with hollow interiors are formed under the complexing effects of potassium sodium tartrate. Numerous mesopores are generated after the precursor is annealed at 500 °C. When applied as anode materials, the mesoporous nanoring-like Zn-Co mixed oxides can deliver a high discharge capacity of 1102 mAh g^{-1} after 200 cycles at 500 mA g^{-1}. Even when the current density is increased to 2 A g^{-1}, the mixed oxides can still retain a reversible capacity of 761 mAh g^{-1}. Such high cycling stability and rate capability are mainly derived from the unique mesoporous ring-like nanostructures and the synergistic effects between Zn and Co based oxides.

1. Introduction

The continually exacerbated environmental problems and impending energy crisis have underscored the urgent need for cleaner and more sustainable energy supply systems [1,2]. Li-ion batteries (LIBs) are regarded as a potential candidate to cope with these imminent issues [3]. However, the low theoretical capacity of graphite anodes (372 mAh g^{-1}) in commercial LIBs has limited their practical application in fields such as electric vehicles, smart grids and large-scale energy storage devices. Thus it is imperative to search for alternative anode materials with larger capacity, higher rate capability and superior cycling stability. Recently, Zn and Co based transition metal

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oxides (TMOs) have been vastly investigated. Monometallic ZnO and Co_3O_4 can deliver theoretical capacities of 978 mAh g^{-1} and 890 mAh g^{-1}, much higher than that of graphite anodes [4,5]. But their application is severely hindered by their poor rate capability and low capacity retention. For Zn and Co based TMOs anodes, the first priority is to find effective methods to improve their rate performance and long-term cycling stability.

Fabricating Zn-Co mixed oxides seems to be an adoptable strategy. For TMOs, mixed oxides can usually incorporate the advantageous properties of the component monometallic oxides, and they may also obtain some unexpected positive features such as higher electronic conductivity, stronger reaction activity and better cycling stability [6,7]. A series of mixed oxides such as NiO@MnO_2 [8], Ni-Co mixed oxides [9], Ag decorated SnO_2-NiO [10], coral-like $Zn_{0.5}Ni_{0.5}Co_2O_4$ [11] and $Ni_{0.9}Zn_{0.1}O$ [12] are reported to exhibit much improved rate and cycling performance. In addition to their high theoretical capacity, Zn and Co based oxides also possess other advantageous features. For zinc based oxides, though monometallic ZnO anodes usually suffer from severe capacity decay in the initial stage, they can maintain a low but stable capacity during the long term cycling test [13,14]. Moreover, zinc oxides are cheap and environmental friendly. For cobalt based oxides, their high catalytic activity is quite favorable for some electrochemical reactions. For example, the high catalytic activity of Co is reported to be helpful in catalyzing the reversible growth of polymeric gel-like films which will positively increase the capacity of electrode materials [15]. So the synergistic mixture between Zn and Co based oxides may well combine these advantages and endow the mixed oxides with a series of desirable electrochemical features.

Besides compositional optimization of Zn-Co based oxides, the rational design of their morphology and structure is also indispensible in achieving high-performance anode materials. Among the various structures, mesoporous hollow nanostructures are quite promising because the mesopores can facilitate the penetration of electrolyte and provide more active sites for reactions; the nanosized structure can shorten the diffusion pathway of Li^+ ions and further increase the surface area; and the hollow interior space can accommodate the large volume expansion during charge-discharge processes [16–18]. However, conventional templating methods to fabricate hollow structures is expensive, and the removal of templates is very difficult to control. Moreover, owing to the high surface energy, the obtained nanosized materials tend to aggregate, which will impede the efficiency of the energy storage process [19]. Thus finding an easy and scalable way to obtain uniformly dispersed mesoporous hollow nanostructures still remains a major challenge.

Inspired by the above considerations, we report herein the template-free synthesis of mesoporous nanoring-like Zn-Co mixed oxides through a simple solvothermal route followed by a subsequent calcination process. The as-prepared Zn-Co mixed oxides have successfully hybridized Co_3O_4, $ZnCo_2O_4$ and ZnO to form a mesoporous ring-like nanostructure with hollow interiors. As a complexing agent, potassium sodium tartrate plays a significant role during the growth of the unique nanostructures. The effects of potassium sodium tartrate on the morphology of the mixed oxides is investigated. With the synergistic effects among the component oxides, the numerous mesopores, nanosized particles and hollow interiors, the mixed oxides exhibit excellent long-term cycling stability and rate capability.

2. Materials and methods

2.1. Material preparation

Analytical-grade $Zn(CH_3COO)_2{\cdot}2H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, potassium sodium tartrate ($C_4H_4O_6KNa{\cdot}4H_2O$) and NH_4HCO_3 were used as received without further purification. Typically, 20 ml deionized water and 40 ml ethylene glycol were mixed as the solvent. 1 mmol $Zn(CH_3COO)_2{\cdot}2H_2O$ and 2 mmol $Co(CH_3COO)_2{\cdot}4H_2O$ were added into the above solvent under magnetic stirring for 30 min. Then 2 mmol potassium sodium tartrate and 15 mmol NH_4HCO_3 were dissolved in the solution. After being magnetically stirred for another 10 min, the resulting mixture was transferred into a Teflon-lined stainless steel autoclave and heated to 200 °C for 24 h. After cooling to room temperature, the precipitate was collected by centrifugation. It was then washed thoroughly by deionized water and absolute ethanol, and dried in air at 60 °C for 12 h. After being calcined at 500 °C in air for 4 h, the mesoporous nanoring-like Zn-Co mixed oxides were obtained and denoted as MO-2. Control samples with potassium sodium tartrate amount of 0, 1, 4, 6 and 8 mmol were also prepared by the same method, and these mixed oxides were denoted as MO-0, MO-1, MO-4, MO-6 and MO-8, respectively.

2.2. Material characterization

X-ray diffraction (XRD, Dmax/2500PC, Rigaku, Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å) was used to characterize the crystallographic structure and phase purity of as-prepared samples. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 spectrometer with Al Kα X-ray source. Field emission scanning electron microscopy (FESEM, JSM-6700F, Japan) is applied to investigate the morphology and structure of the samples. HRTEM images were collected by a FEI-TECNAI G2 F20/America microscope. The chemical composition and elemental mapping images of the sample was obtained with a energy dispersive X-ray spectroscopy (EDS) attached to the FEI-TECNAI G2 F20/America microscope. The nitrogen adsorption and desorption isotherm measurement was carried out on an ASAP 2020 surface area and porosity analyzer.

2.3. Electrochemical measurements

On preparing the working electrode, 70 wt.% active materials with 20 wt.% acetylene black and 10 wt.% sodium carboxymethyl cellulose (CMC) were mixed to form a homogenous slurry. After being uniformly pasted on a copper foil, the electrode materials were dried at 70 °C for 12h in a vacuum oven. CR2025-type coin cells were assembled in an argon-filled glove box. The electrolyte consists of 1 M LiPF6 in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC), and the corresponding volume ratio of EC, EMC and DMC is 1: 1: 1. Li foil was used as the counter and reference electrode. Typical mass loading of the active materials was about 0.8 mg cm^{-2}. Galvanostatic charge–discharge tests were performed in the voltage range of 0.01–3.0 V on a LAND CT2001A battery instrument. A CHI650D electrochemical workstation is used to carry out the cyclic voltammetry (CV) tests in 0.01–3.0V at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectra (EIS) measurements were also recorded on the CHI650D electrochemical workstation with an applied voltage of 5 mV from 0.01 Hz to 100 kHz.

3. Results and discussion

3.1. Structure and morphology

The X-ray diffraction (XRD) patterns of the sample synthesized with 2 mmol potassium sodium tartrate (MO-2) is shown in Fig. 1a. The sharp peaks indicate the high crystallinity of the sample. Most of the diffraction peaks can be assigned to cubic spinel structured Co_3O_4 (JCPDS card no. 42–1467) or $ZnCo_2O_4$ (JCPDS card no. 23–1390). Several weak peaks corresponding to ZnO (JCPDS card no. 36–1451) can be observed. The low peak intensity demonstrates that the content of ZnO is relatively low. Although the standard XRD patterns of Co_3O_4 and $ZnCo_2O_4$ are quite similar, the enlarged patterns in Fig. S1a can help to prove the existence of $ZnCo_2O_4$. As shown in Fig. S1a, the enlarged diffraction peaks of the sample are slightly left shifted compared with the standard patterns of Co_3O_4, and correspond better with the