Chemical Engineering Journal 356 (2019) 1–10

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Template-free synthesis of multifunctional Co_3O_4 nanotubes as excellent performance electrode materials for superior energy storage

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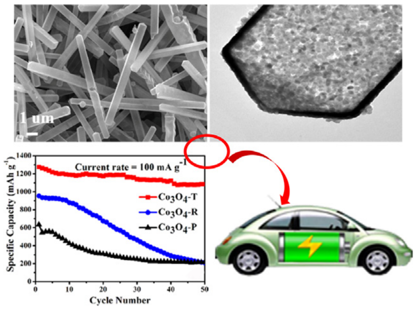
HIGHLIGHTS

- Multifunctional Co_3O_4 nanotubes were prepared by a low-cost and template-free route.
- The tubular structure with small-sized mesoporous can facilitate Li^+ diffusion and enhances structural robustness.
- Excellent cycling stability and rate performances in LIBs and LSBs can be achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Template-free
Co_3O_4 nanotubes
Mesoporous
Li metal batteries

ABSTRACT

Herein, multifunctional Co_3O_4 nanotubes (Co_3O_4-T) are successfully constructed via a low-cost and template-free route, which show a tubular structure with mesoporous and hollow interior. The as-prepared Co_3O_4-T exhibit superior cycling performances, rate capabilities and strong cycling stability when used as the electrode materials in lithium-ion batteries (LIBs) and lithium-sulfur batteries (LSBs). The Co_3O_4-T electrode delivers a high specific capacity of ~1081 mAh g^{-1} at a current density of 100 mAh g^{-1} after 50 cycles in LIBs. Besides, it also shows a high initial discharge capacity of 1049.3 mAh g^{-1} and low overpotential of 154 mV at 0.2 C in LSBs. These excellent electrochemical performances of Co_3O_4-T electrode are attributed to the unique tubular structure with small-sized mesoporous, which facilitates Li^+ diffusion and enhances structural robustness.

1. Introduction

The fast development of portable electronics has stimulated worldwide demand for progressive improvements of energy storage systems [1–4]. Li metal batteries (LMBs), especially lithium-ion batteries (LIBs) and lithium-sulfur batteries (LSBs), possess significant advantages, such as low cost, rapid-rate capability and high energy density compared to other energy storage components [5–9]. However, the large volumetric expansion for LMBs during the lithiation/delithiation process could cause the exfoliation of active materials from current collector and the decrease in specific capacity [10,11]. Thus, it is crucial to seek and design electrode materials with outstanding electrochemical performances for LMBs.

Nanostructured 3d transition-metal oxides have been widely studied as electrode materials, due to their high theoretical specific capacity [12,13]. Among them, cobalt oxide (Co_3O_4) has attracted extensive attention for LIBs, owing to its high theoretical specific capacity (890 mAh g^{-1}), which is nearly three times as high as that of

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https://doi.org/10.1016/j.cej.2018.09.014
Received 9 July 2018; Received in revised form 16 August 2018; Accepted 2 September 2018

commercial graphite (372 mAh g^{-1}), abundance, high corrosion stability, and eco-friendly [13–16]. Importantly, Co_3O_4 as sulfur host materials in LSBs, has strong affinity with lithium polysulfides (LiPSs) and thus keeping them localized on the cathode side to restrain the shuttle effect of LiPSs [11,17,18]. Nevertheless, Co_3O_4 as electrode materials still face some challenges. A large initial irreversible and loss limits rate capabilities owing to large volume expansion, severe particle aggregation and slow Li^+ diffusion during lithiation/delithiation process, which are hampering its widespread commercialization in high performance LIBs and LSBs.

Substantial efforts have been developed electrode materials with unique structure for LMBs to solve these issues. Some structures, such as rod, bulk or sphere structures, generally have no or low porosity, resulting in low active surface areas and poor wettability for electrolytes. By contrast, tubular structure, owing to the advantages of both 1D and hollow structure, is identified as one effective method to solve aforementioned challenges [19]. The presence of hollow tube structure not only provides more space to remit huge volume changes arising from Li^+ insertion/extraction but also shortens the Li^+ diffusion distance, leads to faster reaction kinetics and higher specific capacity [14,20]. These excellent characteristics will endow competitive power in LIBs [20,21]. Additionally, a hollow tube structure, possessing a high surface area and large pore volume, can provide enough spaces and then efficiently encapsulate sulfur, suppress the shuttling of lithium polysulfides as well as improve the utilization of sulfur in LSBs [22,23]. In this regard, the multifunctional Co_3O_4 tubular structure could provide an effective way to solve many drawbacks existing in LMBs and meet the requirements for high-performance energy storage. However, the tubular structure is commonly prepared by template-based strategies or electrophoretic deposition. Chen et al. [19] used carbon fiber as template to obtain Co_3O_4 microtubes for lithium storage. Cui and coworkers [22] reported a coaxial electrospinning method for constructing Co_3O_4 porous nanotube structure. Yoon et al. [24] used single-nozzle electrospinning followed by heating calcination method to get RuO_2/Mn_2O_3 tube as efficient catalysts for lithium-oxygen batteries. Most of these methods often contain complex synthetic process, which are expensive and hinder practical applications for LMBs.

Herein, multifunctional Co_3O_4 nanotubes (Co_3O_4-T) are successfully constructed via a low-cost and template-free route. Specifically, these Co_3O_4 nanotubes are composed of many nanoparticles, which can offer enough active sites, buffer the volume expansion during discharge/charge process as well as efficiently adsorb soluble lithium polysulfides. The well-designed Co_3O_4 nanotubes ensure the enhancement of e^- transfer and Li^+ diffusion. As expected, the as-prepared multifunctional Co_3O_4 nanotubes deliver outstanding electrochemical performances as electrode materials for LIBs and LSBs. The Co_3O_4 nanotubes as anode of LIBs deliver a high specific capacity of 1081.5 mAh g^{-1} at a current density of 100 mA g^{-1} after 50 cycles. In addition, S-Co_3O_4 nanotubes as cathode of LSBs show a high initial specific discharge capacity of 1049.3 mAh g^{-1} and low over potential of 154 mV at 0.2 C.

2. Experimental

2.1. Preparation of Co_3O_4 samples

2.1.1. Synthesis of Co_3O_4 nanotubes

All chemicals were purchased from domestic Chinese suppliers and used as-received without any further purification. 3.74 g $Co(Ac)_2{\cdot}4H_2O$ was dissolved in 15 mL solution (water/ethanol = 1:2, v/v) under ultrasonication for 15 min. Then, the mixture was aged for 72 h at 30 °C. Afterwards, the precursors were harvested by filtering and washing for several times before dried at 60 °C in an oven for 2 h. The Co_3O_4 nanotubes were obtained by annealing precursors under air atmosphere for 1 h at 500 °C with a heating rate of 1 °C min^{-1}.

2.1.2. Synthesis of Co_3O_4 nanoparticles

The synthetic process for Co_3O_4 nanoparticles is same to that of Co_3O_4 nanotubes except solvent (15 mL ethanol).

2.1.3. Synthesis of Co_3O_4 nanorods

0.952 g $Co(Ac)_2{\cdot}4H_2O$ and 0.6 g urea were dissolved in deionized water (40 mL) under vigorous stirring for 0.5 h. This homogeneous solution was transferred into a 50 mL Teflon-sealed autoclave and kept at 95 °C for 6 h. After being cooled down to room temperature, the products were collected and washed with deionized water and ethanol for several times, then dried at 60 °C for 2 h and annealed at 400 °C for 2 h in air to obtain final product Co_3O_4 nanorods.

2.2. Characterization

The as-prepared samples were characterized by X-ray diffraction (XRD, Rigaku SmartLab 9KW diffractometer with Cu K), ultrahigh-resolution scanning electron microscope with FEG (SEM, FEI Verios 460L), transmission electron microscope (TEM, Tecnai G2 Spirit TWIN, FEI), high-resolution TEM with FEG (HRTEM, Talos F200X, FEI), and thermogravimetry analysis (TGA, Netzsch TG 209 F3). Brunauer–Emmett–Teller (BET) surface areas of all samples were determined through N_2 adsorption/desorption isotherms at 77 K collected (Quantachrome iQ-MP gas adsorption analyser). The surface component of all samples were tested by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

2.3. Electrochemical measurements

2.3.1. The assembling and testing of LIBs

The working electrodes were composed of active materials, acetylene black (AB), and polyvinylidene fluoride (PVDF) at the weight ratio of 80: 10: 10. The average weight of active materials was ~1.5 mg. Lithium metal was used as the counter electrode. 1 M $LiPF_6$ dissolved in a 1:1:1 mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC) was used as electrolyte. Coin cells were assembled in a glove box filled with high-purity argon. The discharge/charge voltage were performed between 0.01 and 3.0 V (vs. Li/Li^+ Li^+/Li) under a LAND-CT2001A instrument at room temperature. The specific capacity was calculated according to the corresponding total weight of active materials in each electrode.

2.3.2. The assembling and testing of LSBs

The Co_3O_4 samples and sulfur with a weight ratio of 1:3 were dissolved into 20 mL CS_2 under high power ultrasonic until CS_2 was completely evaporated. The obtained S-Co_3O_4 mixture was heated at 155 °C for 16 h under Ar atmosphere.

The S-Co_3O_4 electrodes were prepared by mixing the S-Co_3O_4 mixture, Super P and PVDF with a weight ratio of 70: 20: 10 in an N-methyl-2-pyrrolidone solvent. The obtained S-Co_3O_4 electrodes contained ≈1.0 mg cm^{-2} of sulfur. Coin cells consisting of a lithium metal anode, Celgard 2400 separator and the S-Co_3O_4 electrodes were assembled in an argon-filled glovebox. The electrolyte used was LiTFSI (1 M) and 1% $LiNO_3$ dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 vol). The current rate set for tests was referred to the mass of sulfur in the electrodes. The charge-discharge voltage range was 1.7–2.8 V. The frequency range of the EIS measurements was 100 kHz–10 mHz with an AC voltage amplitude of 5 mV at the open-circuit potential.

3. Results and discussion

Scanning electron microscopy (SEM) images (Fig. 1A and B) show that the obtained Co_3O_4 materials have uniform tubular morphologies with a length of 9 µm and a diameter of 500 nm. Interestingly, the ends of Co_3O_4 nanotube is a tetrahedron structure. The breakage of