



Cobalt carbonate dumbbells for high-capacity lithium storage: A slight doping of ascorbic acid and an enhancement in electrochemical performances



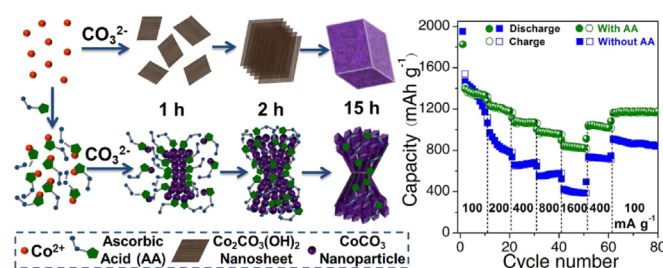
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HIGHLIGHTS

- CoCO_3 dumbbells are hydrothermally synthesized in the presence of ascorbic acid.
- The crystallization and aggregation of CoCO_3 are greatly modified by ascorbic acid.
- Ascorbic acid doped CoCO_3 dumbbells exhibit enhanced electrochemical performances.
- The 100th discharge capacity is as high as 1042 mAh g^{-1} at 200 mA g^{-1} .

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of materials with desirable nanostructures is a hot research topic owing to their enhanced performances in contrast to the bulk counterparts. Herein, dumbbell-shaped cobalt carbonate (CoCO_3) nano architectures and the bulk counterpart of CoCO_3 rhombohedra are prepared via a facile hydrothermal route in the presence and absence of ascorbic acid (AA), respectively. By comparison, it has been found that: the addition of AA in the hydrothermal crystallization system changes the shape of the building blocks from $\text{Co}_2\text{CO}_3(\text{OH})_2$ nanosheets to CoCO_3 nanoparticles, and then further influences the final configuration of the products. When applied as anodes of lithium ion batteries, CoCO_3 dumbbells deliver a 100th capacity of 1042 mAh g^{-1} at 200 mA g^{-1} and even exhibit a long-term value of 824 mAh g^{-1} over 500 cycles at 1000 mA g^{-1} , which are much higher than the rhombohedral counterparts with corresponding 540 and 481 mAh g^{-1} respectively. The much higher capacity, better cycling stability and enhanced rate performance of CoCO_3 dumbbells can be attributed to the higher specific surface area, smaller charge transport resistance and better structure stability resulting from the slight doping ($\sim 4.6 \text{ wt\%}$) of AA, and also relate with a novel lithium storage mechanism in CoCO_3 .

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1. Introduction

Non-renewable fossil fuels are still the main energy sources nowadays, but bring serious environmental pollution when used.

Thus, the development of clean and renewable energy sources and storage devices has been recognized as an effective solution for the energy and environmental crises [1–3]. As one of the most promising energy storage devices, rechargeable lithium ion batteries (LIBs) possess the considerable advantages of high energy density, long lifespan and good environmental benignity, and have enjoyed a great commercial success in portable electronics such as cell

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phones, notebook computers and so on [4]. However, LIBs can hardly satisfy the ever-growing requirements of large-scale high-energy applications such as electric vehicles and smart grids. Considering the low theoretical capacity of graphite (i.e., 372 mAh g⁻¹) for the commercial LIBs, the development of novel advanced anode materials with high capacity is crucially important [5,6].

As a new kind of available lithium storage materials, transition metal carbonates (MCO₃, M = Co, Mn, Fe) have been hot research focuses in recent years due to their facile synthesis, high specific capacities and good electrochemical durabilities [7–20]. It has been proved that the practical capacities of some MCO₃ products are as high as or even higher than the corresponding transition metal oxides (MO) [7,9,10,18,20]. For example, the 10th reversible capacity of microspindle-like CoCO₃ could reach 1065 mAh g⁻¹, higher than that of microspindle-shaped CoO (~720 mAh g⁻¹) operated at a same rate of 50 mA g⁻¹ [18]. More interestingly, most of the reported capacities of MCO₃ are higher than the calculated theoretical capacity (~450 mAh g⁻¹) according to the traditional conversion reaction mechanism (MCO₃ + 2Li ↔ Li₂CO₃ + M), which indicates there must be novel mechanisms for lithium storage in MCO₃ [7–10]. In the previous studies about CoCO₃, the extra-capacity contribution has been assigned to the reversible redox reaction between C⁴⁺ in CO₃²⁻ and its low valence states (e.g., C⁰) under the catalysis of in-situ generated transition metal nanocrystals [9,10,18,21–25]. To analyze the galvanostatic discharge-charge behaviors of MnCO₃ electrodes, both Faradaic and non-Faradaic (capacitance) contributions were briefly summarized to reveal the ambiguous reaction mechanism of MCO₃ towards metallic lithium [11,16,17]. In view of the extremely high lithium storage capability of micro-rhombohedral FeCO₃ (e.g., the 120th reversible capacity ~1018 mAh g⁻¹, 200 mA g⁻¹), the unexpectedly detected ferric derivatives coming from the further oxidation of ferrous origins were mentioned, which could partly explain the excellent electrochemical properties of FeCO₃ micro-rhomboheda [7]. Furthermore, the extra contributions of conductor acetylene black, polymeric binder and gel-like layer formed at the particles' surface should not be omitted to analyze the acquired high-capacity of the active substances [26–29].

However, the reported MCO₃ materials with usual bulk structures (e.g. microcube, microsphere) mainly express unsatisfactory lithium storage capabilities due to their bad electronic conductivities or structural stabilities. Thus, conductive additives such as carbon nanotube (CN), conductive polymer and graphene are widely incorporated to improve the electronic conductivity of MCO₃ [9,10,13,30,31]. The resulted composites of MnCO₃/CNs, CoCO₃/polypyrrole and CoCO₃/graphene exhibited a satisfactory retention capacity of ~647 (100th, 100 mA g⁻¹), 1070 (100th, 100 mA g⁻¹) and 930 mAh g⁻¹ (40th, 50 mA g⁻¹), respectively [9,10,13]. Besides, benefiting from the unique structural features, the designedly synthesized rambutan-like FeCO₃ hollow microspheres assembled by nanofibers could also deliver a satisfactory reversible capacity of 710 mAh g⁻¹ after 200 cycles at 200 mA g⁻¹ [8]. These all suggest that an optimally designed synthesis and its endowed improved structural properties are of crucial importance for the practical application of MCO₃ in LIBs.

In this paper, CoCO₃ dumbbells are synthesized from a simple aqueous system of cobalt acetate and ammonium carbonate in the presence of AA which express much better lithium storage performances in contrast to the rhombohedral CoCO₃ counterpart obtained in the absence of AA. Aside from the contrastive hydrothermal formation processes of CoCO₃ rhombohedron- and dumbbell-shaped architectures, the structure–function relationships and the resulted enhanced lithium storage capabilities of CoCO₃ dumbbells doped by a little AA (~4.6%) are the main topics.

2. Experimental

2.1. Material preparation

All the chemicals are of analytic grade and were used as received. At first, solid-state cobalt acetate tetrahydrate Co(Ac)₂·4H₂O (1.0 mmol) and ammonium carbonate (NH₄)₂CO₃ (5.0 mmol) were dissolved in 30 and 10 mL ultrapure water (18.2 MΩ cm), respectively. Then, solid-state ascorbic acid (AA, 1.0 mmol) was dissolved into the Co(Ac)₂·4H₂O solution. After that, the (NH₄)₂CO₃ solution was dropwise added into the Co(Ac)₂·4H₂O solution under a vigorous stirring. The resulting suspension was transferred into a 50-mL Teflon-lined autoclave, which was sealed and allowed to stand still in a thermostatic chamber at 160 °C for 15 h. Finally, the autoclave was cooled to room temperature, and the obtained CoCO₃ dumbbell-shaped crystallites were collected by centrifugation, washed with ultrapure water and absolute alcohol for 3 times respectively and then dried at 80 °C for 10 h. In contrast, CoCO₃ rhombohedral counterparts were obtained in the absence of AA.

2.2. Material characterization

Field-emission scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700F microscope operating at 15 kV. X-ray diffraction (XRD) measurements were performed using a Rigaku D/max-2400 powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å, 40 kV, 120 mA). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under air atmosphere with a heating step of 10 °C min⁻¹ from room temperature to 800 °C. Samples were dispersed in ethanol by ultrasonication and then deposited on a carbon film supported by the copper grid, prior to transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) measurements on a JEM 2100 microscope (200 kV). Nitrogen (N₂) adsorption-desorption were conducted on a Micromeritics ASAP 2020 sorptometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Scientific ESCALAB 220i-XL electron spectrometer with Al Kα radiation.

2.3. Electrochemical measurements

After dispersing synthetic CoCO₃, acetylene black and sodium alginate at a weight ratio of 7:2:1 in ultrapure water, the resulting slurry was pasted onto a copper foil and dried at 80 °C for 12 h. And then, the foil was cut into discs (12 mm in diameter) and used as working electrodes with a loading density of 1.5 ± 0.2 mg cm⁻². Lithium metal, nickel foam, Celgard 2300 microporous membrane and commercial LBC 305-01 LiPF₆ solution (Shenzhen Xinzhou-bang) were used as counter electrode, current collector, separator and electrolyte, respectively. CR2032-type coin cells were assembled in an argon-filled glove box. Galvanostatic cycling tests were conducted on an LAND CT2001A system (Wuhan Landian) within 0.01–3.0 V (vs. Li⁺/Li). Cyclic voltammetry (CV) curves were collected on an LK 2005A Electrochemical Workstation (Tianjin Lanlike) at 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (Materials Mates 510, Italia) in the frequency range from 0.1 MHz to 0.01 Hz.

3. Results and discussion

3.1. The effect of doping AA on the crystal growth of CoCO₃

Fig. 1 shows SEM images (Fig. 1a, b), XRD patterns (Fig. 1c), TGA-DSC curves (Fig. 1d) of the obtained CoCO₃ rhombohedra and

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