



Short communication

Hollow Co_3O_4 thin films as high performance anodes for lithium-ion batteries

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ABSTRACT

Cobalt oxide thin films composed of hollow spherical Co_3O_4 particles have been prepared by a two-step method. The first step involves in the synthesis of hollow cobalt alkoxide particles in a stable suspension from mixed polyalcohol solutions of cobalt acetate in oil bath at 170°C . The second step includes the thin film fabrication by electrostatic spray deposition (ESD) and subsequent heat treatment in nitrogen. The obtained Co_3O_4 films with the unique hollow particle microstructure exhibit high reversible capacity of above 1000 mAh g^{-1} during up to 50 cycles and good rate capability. The films are promising negative electrodes for high energy lithium-ion batteries.

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1. Introduction

The high performance lithium-ion batteries (LIBs), which have been applied widely already in portable devices and power tools and increasingly in pure or hybrid electric vehicles, are regarded as the crucial and realistic power sources [1,2]. In order to address the needs of these modern electronic devices and broader applications, recent researches focus on the better electrode materials for the improvement of LIBs, such as better cycle performance and rate capability, higher capacity as well as high energy density [3–7]. Transition-metal oxides are attractive candidates of anode materials owing to their high Li storage capacity [8–10], but in the meantime, they are disadvantageous with large (usually over 35%) initial irreversible capacity loss and poor capacity retention [11–13]. The use of nanostructured thin-film electrodes has been proved to be an effective way to improve above drawbacks [9,14,15].

Electrostatic spray deposition (ESD) is an available method to prepare highly reticular or porous thin films for various anode and cathode materials of lithium-ion batteries without extra binder and conductive matters [5,9,16,17]. In this study, cobalt oxide thin films composed of hollow spherical Co_3O_4 particles are synthesized by the ESD technique, which uses a stable alkoxide suspension instead of a commonly used solution as the precursor. These films with the unique microstructure exhibit an high reversible capac-

ity of above 1000 mAh g^{-1} with a relatively low initial capacity loss.

2. Experimental

Cobalt hydrated acetate ($\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$) was dissolved in five mixed solvents of ethylene glycol (EG) and 1,2-propanediol (1,2-Pr) with volume ratios of EG:1,2-Pr = 1:0, 3:1, 1:1, 1:3, 0:1 to produce 0.01 M solutions. Then, the solutions were heated at 170°C by a silicone oil bath under vigorous magnetic stirring for 2 h. After cooling down to room temperature, stable precursor suspensions were obtained. For structural analysis, some violet powders were collected by centrifugation and washed with absolute ethanol for several times. With one of the suspensions, where 1,2-Pr:EG = 1:1, as the precursor for ESD process, thin films were fabricated on copper foils that were heated at 290°C . The applied voltage was 10–11 kV between the substrate and the nozzle that was connected to a syringe pump to deliver the precursor suspension at a rate of 1.8 ml h^{-1} for 3–4 h. The distance between nozzle and substrate was 3 cm.

The powder morphology was observed under a scanning electron microscope (SEM, JEOL, JSM-6390LA) and a transmission electron microscope (TEM, Hitachi H-800). All the samples were analyzed by X-ray diffraction (XRD) with a diffractometer (Philips X'Pert Pro Super, $\text{Cu K}\alpha$ radiation). The electrochemical behavior of the thin films was examined using CR2032 coin type cells vs. Li with 1 M LiPF_6 in ethylene carbonate and diethyl carbonate (EC:DEC = 1:1, v/v) as the electrolyte. The cells were assembled in an argon-filled glove box (MBraun Labmaster 130). They were cycled

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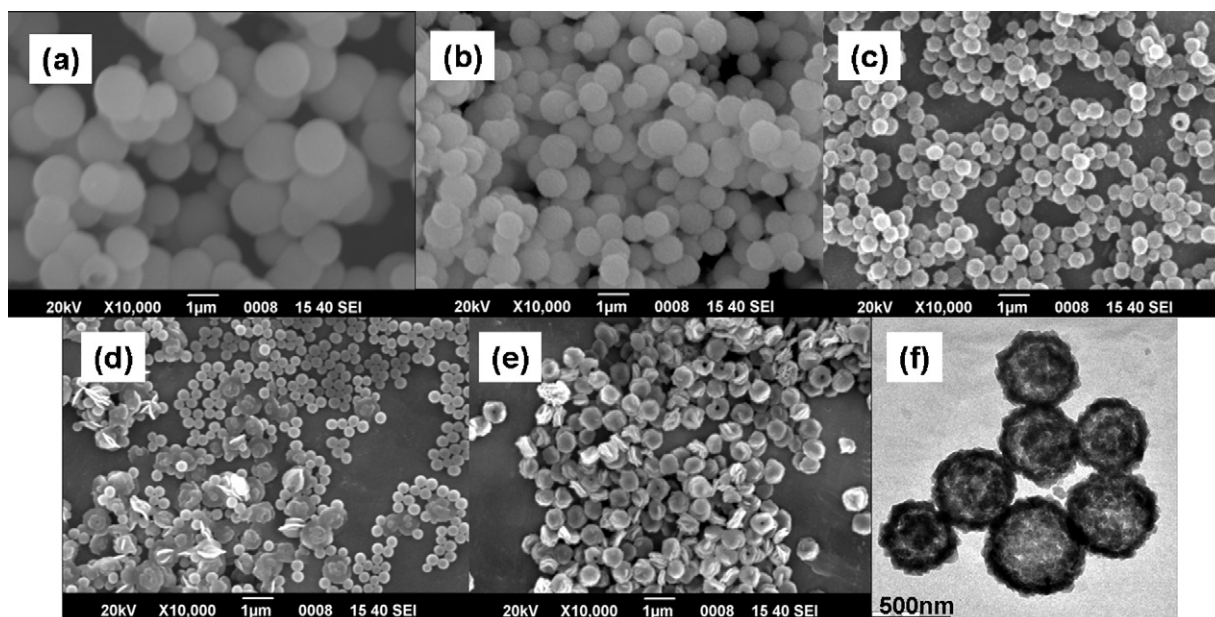


Fig. 1. SEM and TEM image of powder synthesized in different ratio of 1,2-propanediol (1,2-Pr) and ethylene glycol (EG) at 170 °C for 2 h: (a) pure 1,2-Pr, (b) 1,2-Pr: EG = 3:1, (c) 1,2-Pr: EG = 1:1, (d) 1,2-Pr: EG = 1:3, (e) pure EG, (f) 1,2-Pr: EG = 1:1.

in the voltage range between 3.0 and 0.01 V at a current density of 0.2 mA cm⁻² on a battery test system (Neware BTS-610).

3. Results and discussion

Fig. 1 displays the particle morphology of the powders synthesized in different solvents. It can be seen that rather monodisperse spherical particles are obtained when the content of 1,2-Pr is 100%, 75% and 50%, respectively (Fig. 1a–c). The diameter of the spheres decreases with decreasing the 1,2-Pr content and increasing the EG content. Such a trend in the change of particle size is consistent with Tarascon et al.'s results [18]. Nevertheless, in their study, they still obtained spherical particles when pure EG was the solvent although other morphologies such as polyhedra and platelets were obtained when using 1,3-propanediol and glycerol as solvents. In our study, however, when the content of 1,2-Pr decreases to 25%, the synthesized powder shows coexistence of spheres and plates (Fig. 1d). Furthermore, when prepared in pure ethylene glycol solvent, the obtained powder is composed of many donut-like round plates (Fig. 1e). Obviously, the nature of the polyalcohol medium has a major impact on the size and morphology of the formed particles because different polyalcohols have different physical properties like surface tension and viscosity that can affect the nucleation and crystal growth of the particles. For example, the surface ten-

sion of 1,2-Pr (0.072 N m⁻¹, 25 °C) is greater than EG (0.048 N m⁻¹, 25 °C). In order to have a stable precursor suspension for the next ESD step, the one with 1,2-Pr:EG = 1:1 is selected; the powder in the suspension has small particle sizes (300–500 nm) and uniform morphology (Fig. 1c).

The XRD pattern of the powder obtained in the suspension (Fig. 3a) exhibits a strong diffraction peak at low-angle region (around 10°) and other weak peaks at 16°, 24°, 31° and 34°. It is almost the same as the pattern for cobalt alkoxide prepared with pure 1,2-Pr as the solvent [18], indicating that the powder is also a cobalt alkoxide. Its infrared spectrum gives the bands located below 2000 cm⁻¹ due to metal–O, C–C, C–O, and CH₂ bonds (Fig. 2a). Signals due to C–H and hydrogen-bound OH vibrations are also detected. This infrared result also confirms partly the formation of the cobalt alkoxide.

As can be seen from the TEM analysis (Fig. 1f), these particles are clearly found to have hollow structures with either void or another smaller shell in the interior space. Note that, Tarascon et al. or other groups have never reported such a hollow structure for an alkoxide powder thus obtained. With larger magnifications, the shells are actually nanoporous and composed of some smaller grains (Fig. 2b). Ostwald ripening is an appropriate mechanism to explain the formation of these structures [19]. But both “outward ripening” (mass transport starts from center) and “inward ripening”

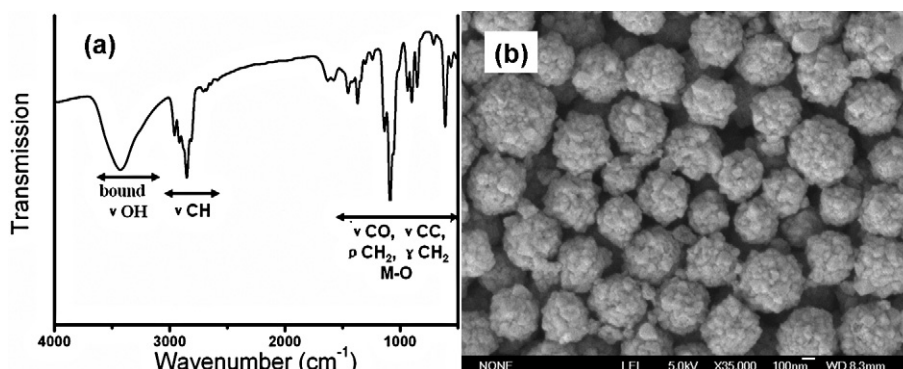


Fig. 2. Infrared spectrum of the cobalt alkoxide powder (a) and SEM image of the powder with larger magnifications (b).

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