



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 1000mAh 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 1000mAh 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, Cu $\text{K}\alpha$ 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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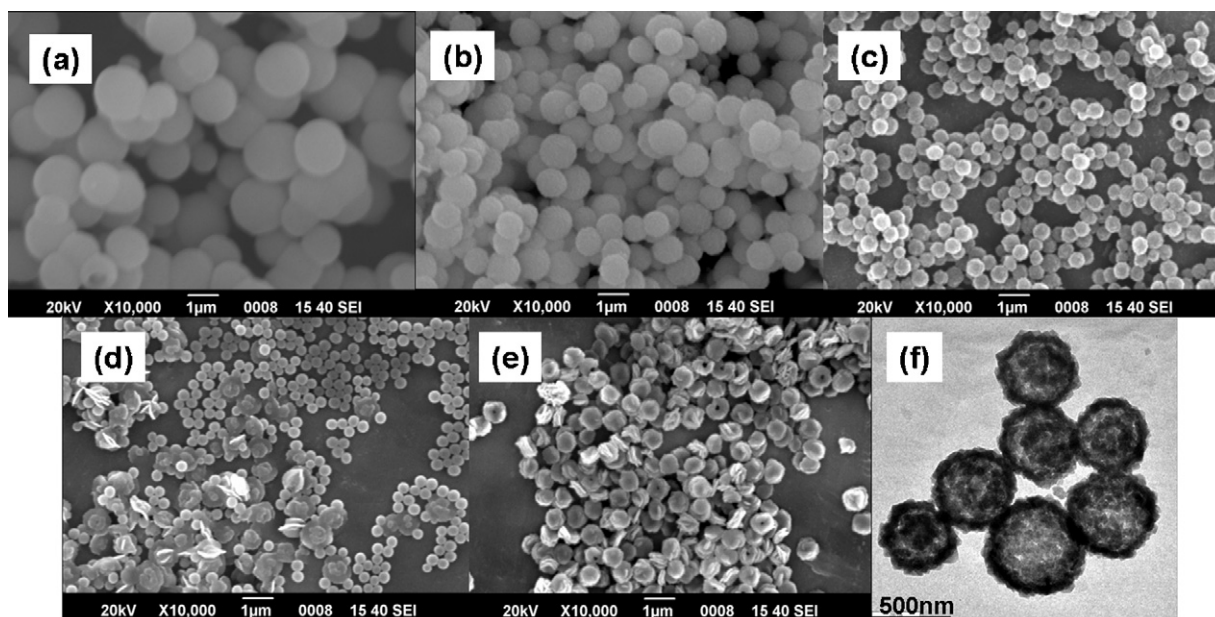


Fig. 1. SEM and TEM image of powder synthesized in different ratio of 1,2-propanediol (1,2-Pr) and ethylene glycol (EG) at 170 °C for 2 h: (a) pure 1,2-Pr, (b) 1,2-Pr: EG = 3:1, (c) 1,2-Pr: EG = 1:1, (d) 1,2-Pr: EG = 1:3, (e) pure EG, (f) 1,2-Pr: EG = 1:1.

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 CH_2 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”

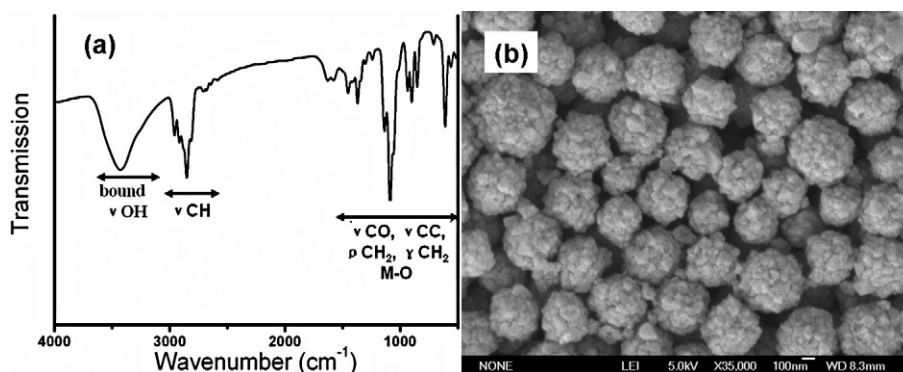


Fig. 2. Infrared spectrum of the cobalt alkoxide powder (a) and SEM image of the powder with larger magnifications (b).

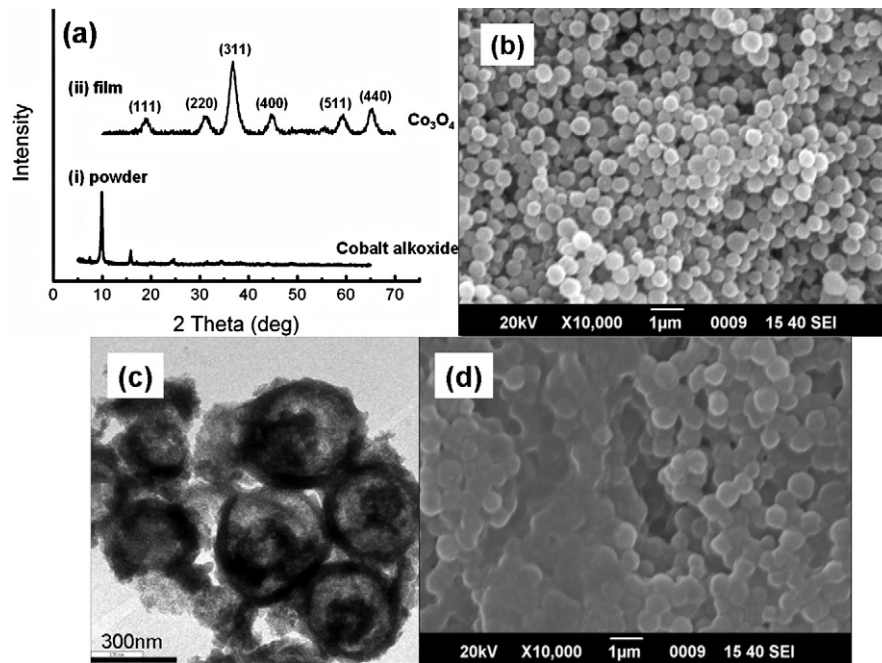


Fig. 3. XRD patterns of the cobalt alkoxide powder and the film deposited at 290 °C (a); SEM and TEM image of Co_3O_4 film (b and c); SEM image of Co_3O_4 film after 50 cycles (d).

(mass transport starts from surface) must be combined to create the various interior structures. From these hollow cobalt alkoxide particles, we can prepare the hollow cobalt oxides that are most desirable as the active electrode materials for lithium-ion batteries because the intrinsically large volume change of the electrode during the charge-discharge process can be digested with such a structure without causing electrode detachment from the current collectors.

With the above suspension as the precursor, a cobalt oxide thin film can be fabricated on copper foil substrate by means of ESD under ambient atmosphere. The XRD analysis of the powder that is scraped from the film shows that the film is actually pure Co_3O_4 (Fig. 3a). After the ESD process, the hollow spherical particle structures are still maintained (Fig. 3b and c). The film is composed of interconnecting spherical particles. Owing to the evaporation and decomposition of the organic ingredients in the original alkoxide particles, the mean particle size in the Co_3O_4 thin film is about 300 nm (Fig. 3c), slightly smaller than that of the alkoxide particles (Fig. 1c).

With the hollow Co_3O_4 thin film as the working electrode in a half-cell versus lithium metal, its electrochemical properties can be evaluated (Fig. 4). Obviously, such a Co_3O_4 thin film exhibits excellent performance in terms of high specific capacity, good cycling stability and relatively low initial capacity loss. It can deliver a specific capacity of $1424.3 \text{ mAh g}^{-1}$ in the first-discharge step, and the initial capacity loss is 24.9%. The first-discharge voltage profile of thin film shows the typical characteristics of Co_3O_4 electrodes, that is, a long flat voltage plateau at about 1 V and followed by a sloping curve down to the cut off voltage 0.01 V (Fig. 4a). After the first discharge, because of a heterogeneous reaction mechanism of lithium insertion and extraction, the flat plateau is substituted by a sloping curve. The reaction mechanism of the Co_3O_4 electrode can all be explained by the so-called “conversion reaction”, like other transition-metal oxides [8,20]. Nevertheless, CoO phase instead of Co_3O_4 is formed at the end of charging step [21]. Note that the first-discharge capacity values measured here ($1424.3 \text{ mAh g}^{-1}$) are higher than the theoretical capacity predicted by the conversion reaction mechanism, i.e. 890 mAh g^{-1} for Co_3O_4 . The extra capac-

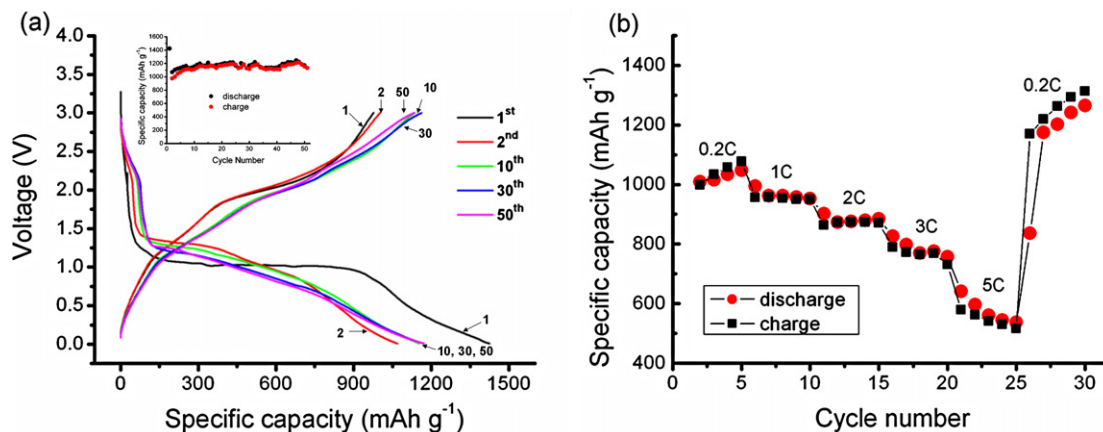


Fig. 4. The electrochemical performance of Co_3O_4 film electrodes: (a) voltage profile and cycling performance at a current density of 0.2 mA cm^{-2} , (b) rate capability.

ity may be due to the gel-like polymer film formed on the particles surface [22]. After 50 cycles, the reversible discharge capacity is $1171.4 \text{ mAh g}^{-1}$, corresponding to 82.2% of the initial capacity (the contribution from copper oxide is about $60\text{--}80 \text{ mAh g}^{-1}$) (Fig. 4a). In addition, the cell shows good rate capability with average discharge capacity of 1015 mAh g^{-1} at 0.2 C, 966 mAh g^{-1} at 1 C, 883 mAh g^{-1} at 2 C, 786 mAh g^{-1} at 3 C, 576 mAh g^{-1} at 5 C and then the capacity go back to above 1100 mAh g^{-1} at 0.2 C (Fig. 4b).

The excellent high capacity, cycle performance and good rate capability of Co_3O_4 films are mainly attributed to their structure. To a large extent, the volume changes during the cycles are controlled by void interior space of particles. After 50 cycles, the morphology of the spherical particles in the film is still maintained, but the particle size has been increased to about 700 nm (Fig. 3d). The increase in the particle size should be mainly resulted from the effect of volume expansion due to the conversion reaction $\text{Co}_3\text{O}_4 + 8\text{Li} \rightarrow 3\text{Co} + 4\text{Li}_2\text{O}$ and, to a lesser extent, from the SEI layer formation or incomplete decomposition of the gel-like film on the particle surface.

4. Conclusions

Cobalt oxide thin films composed of hollow Co_3O_4 spheres can be prepared by ESD technique with a precursor suspension of cobalt alkoxide with also a hollow structure. The unique structure can control the volume change in electrochemical cycling to protect the electrode integrity. The thin films have low initial capacity loss, stable cycle performance, high specific capacity and good rate capability. These Co_3O_4 thin films can be candidates of negative electrode materials for high energy density lithium-ion batteries.

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