



Morphology controllable synthesis and electrochemical performance of LiCoO₂ for lithium-ion batteries



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ABSTRACT

In this work, morphology-controlled lithium cobalt oxides (LCO) were obtained by a simple two-step method that involves a Co₃O₄ synthetic process, in which cubic and spherical Co₃O₄ were prepared by a hydrothermal method and a subsequent lithiation process with Li₂CO₃. The structures and morphologies of two materials were investigated by XRD, SEM and TEM. In contrast with the LCO prepared by using commercial Co₃O₄ precursor, the cubic and spherical LCO materials have an excellent performance in cyclic stability and rate capacity which is attributed to the better fluidity and less agglomeration with specific morphology of LCO materials.

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1. Introduction

LiCoO₂ has been widely applied as one of the most attractive cathode materials in the field of lithium-ion batteries due to its unique advantages including superior cyclic stability, excellent cycle life, high open circuit voltage and easy preparation [1]. By now, LiCoO₂ has been researched for tens of years and largely used in the field of commercial applications. Although it has a few disadvantages, such as high price and toxicity, LiCoO₂ still has an important role in the market of cathode materials. People's attentions to LiCoO₂ have not been cooled down, and lots of studies about LiCoO₂ have been reported in recent years [2–9].

Morphology control of particles for cathode materials plays an important role in material packing density. Powder materials with irregular morphologies are prone to be agglomerated and “bridge formation”, which results in a number of vacancies among particles and reduces the fluidity of the particles [10]. In contrast, materials with specific morphology particles have the advantage of high packing density and specific volumetric capacities. When the particles have an ideal size distribution, the smaller particles could fill up the gaps among large particles and the stacking density

increases, which is helpful for achieving high energy density in lithium ion batteries. According to Ying's study [11], the tap-density of powder LiCoO₂ are usually 2.2–2.4 g cm⁻³, which limits the energy density of LiCoO₂ materials. Furthermore, the materials have better dispersity and fluidity, which are beneficial to be the electrode materials. The materials with regular morphologies are easier for further modification by uniform and stable coated layer. Many materials with regular particles [12–15] exhibited better electrochemical performance than the materials with irregular particles. Therefore, morphology controllable particles are the tendency in the development of industrial production for lithium-ion batteries.

In recent years, persons pay more attentions to morphology control for cathode materials. Various electrode materials, such as nanoparticles, nanowires, nanotubes, hollow cubes and hollow spheres, have been reported [16–20]. For example, Xiao et al. [17] synthesized uniform LiCoO₂ nanoplates with a capacity of 113 mAh g⁻¹ at a rate of 1000 mA g⁻¹ after 100 cycles. Hao et al. [21] prepared single-crystalline LiMn₂O₄ hollow nanocones via a template-engaged reaction, which maintained a capacity of 100 mAh g⁻¹ even at a high rate of 50C and retained 94.8% after over 1000 cycles at 5C. Xiao et al. [18] prepared LiCoO₂ nanowires composed of nanoparticles, which showed excellent rate capability, and its capacity retention was higher than 80% after 100 cycles

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at a high rate of 1000 mA g^{-1} . Our group [16] has also made an attempt on the synthesis of porous sphere $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via an impregnation method and the material showed much better electrochemical properties than that synthesized by commercial source and conventional approaches. All these have demonstrated that materials with specific morphologies are beneficial to the electrochemical performance of cathode materials in Li-ion batteries.

Considering above-mentioned reasons, the cubic and spherical LiCoO_2 were synthesized by a solid phase method using morphology controllable Co_3O_4 obtained by a simple hydrothermal method as engaged template in this work. The cubic and spherical LiCoO_2 is in a size range of $10 \sim 15 \mu\text{m}$. Such big particles can reduce the contact area and weaken the side reactions on interfaces between electrolyte and electrode. Resultantly, both cubic and spherical LiCoO_2 showed excellent performance in cyclic stability and rate capability.

2. Experimental

2.1. Material preparation

Cubic Co_3O_4 synthesis (a modified hydrothermal method [22]): 1.70 g cobalt acetate, 2.10 g urea and 1.40 g triethanolamine were dissolved in 70.0 ml deionized water. After stirring for 1 h, the mixed solution was transferred to a 100 ml teflon-lined stainless steel autoclave. The autoclave was kept at 160°C for 12 h, and then cooled naturally to the room temperature. The prepared pink powders were first filtered and washed for more than three times by deionized water and ethanol, then dried in the electric oven at 110°C for 3 h, and finally calcined in muffle furnace at 600°C for 10 h with a heating rate of $10^\circ\text{C min}^{-1}$.

Spherical Co_3O_4 synthesis (a modified hydrothermal method [23]): 1.00 g cobalt chloride hexahydrate and 2.00 g urea were dissolved in a mixture solution of 20.0 ml deionized water and 60.0 ml glycerol, after stirred to transparent, the mixed solution was transferred to a 100 ml teflon-lined stainless steel autoclave. The autoclave was kept at 120°C for 12 h, and then cooled naturally to the room temperature. The prepared pink powders were firstly filtered and washed for more than three times by deionized water and ethanol, then dried in the electric oven at 110°C for 3 h, and finally calcined in muffle furnace at 600°C for 10 h with a heating rate of $10^\circ\text{C min}^{-1}$.

The Co_3O_4 prepared above was mixed with appropriate Li_2CO_3 by a grinding process and calcined in air at 850°C for 12 h with a heating rate of 2°C min^{-1} , then cooled down to room temperature slowly. The obtained LCO maintained the morphology of Co_3O_4 . The LCO sample using cubic Co_3O_4 as cobalt source was denoted as cubic-LCO, while that using spherical Co_3O_4 was marked as spherical-LCO.

In order to make a contrast with this two regular shaped LCO, the LCO using commercial Co_3O_4 materials (99.99% aladdin) as cobalt source were synthesized in the same condition, which is labelled as powder-LCO.

2.2. Material characterization

The XRD patterns were collected on a Rigaku miniflex 600 instrument equipping with $\text{Cu K}\alpha$ radiation operated at 40 kV and 15 mA from 10° to 90° at 2° min^{-1} with a recording interval of 0.02° . Field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphologies of samples. Transmission electron microscopy (TEM, JEOL-2100) was used to confirm the morphologies and identify the structures of the as-prepared samples. The particle sizes were analyzed by Malvern laser particle size analyzer (Mastersizer2000).

2.3. Electrochemical measurements

The electrochemical properties were evaluated in CR2016-type coin-cell configuration. The active materials were mixed with acetylene black and polyvinylidene difluoride (PVDF) (weight rate 80: 10: 10) in N-methyl pyrrolidone. The slurry was spreading onto an aluminum foil and dried in a vacuum oven at 80°C overnight. The electrodes were punched out and roll-pressed. The coin cells were assembled in an argon-filled glove box (MBraun, Germany). The lithium metal foil was as the counter electrode and the polypropylene membrane (Celgard 2400) was as the separator. The electrolyte used was 1 mol L^{-1} LiPF_6 salt dissolved in a mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1: 1.

The charge-discharge tests were performed on LAND battery test system (CT-2100A, Wuhan, China) in the voltage window $3.0 \sim 4.3 \text{ V}$ at room temperature. The charge process was involving constant current charge and constant voltage charge [24]: the constant current charge step to the desired voltage and the constant voltage charge was executed till the current decreased to one tenth of the constant current value. The electrochemical impedance spectra (EIS) were performed on Solartron (SI 1287) electrochemical workstation with a frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

The morphologies and structures of LiCoO_2 and Co_3O_4 were characterized by SEM, XRD and TEM. The SEM images of cubic and spherical Co_3O_4 precursors are shown in Fig. 1. The cubic samples possess regular and uniform mesoporous structure with diameters of about $10 \sim 15 \mu\text{m}$ (Fig. 1a and b). The micron-size particles are stacked by nano-sheet layers and each layer is consisted of irregular nanoparticles with diameters of about $50 \sim 200 \text{ nm}$ assembling together. The spherical samples (Fig. 1c and d) show uniform spherical structure with diameters of about $10 \sim 15 \mu\text{m}$ which are accumulated by small cubic particles that are further composed of nanoparticles with diameters of about $50 \sim 100 \text{ nm}$. After blending and calcining with lithium carbonate, the LCO were obtained. Fig. 1e and f show that the obtained cubic LCO particles with diameters of $10 \sim 15 \mu\text{m}$ are consisted of dense particles with diameters of about $0.5 \sim 1 \mu\text{m}$. Fig. 1g and h indicate that the spherical LCO samples with diameters of $10 \sim 15 \mu\text{m}$ are also composed of dense particles with diameters of about $1 \sim 2 \mu\text{m}$. The SEM images indicate that the LCO inherit the Co_3O_4 morphology successfully with uniform distribution in size and the less pores can be seen on the surfaces. The sizes of particles were also analyzed by Malvern laser particle size analyzer (Fig. 2), and the results are consistent with the SEM results. In comparison, commercial Co_3O_4 are consisted of uniform and irregular particles (Fig. 1i) and the obtained powder-LCO (Fig. 1j) using commercial Co_3O_4 as cobalt source are composed of pulverous particles (about $0.5 \sim 1 \mu\text{m}$) without specific morphology. Moreover, some agglomeration phenomena of particles exist in the powder-LCO material. The particle size of the powder-LCO was analyzed as shown in Fig. S1. It can be seen that the particle size of powder-LCO is around 100 nm and $3 \sim 5 \mu\text{m}$. The nanoparticles may be the broken ones. Also a few particles are in size of about $20 \sim 30 \mu\text{m}$, it could be attributed to the agglomeration of particles. It is tested that the tap-density values of cubic and spherical LCO are 2.63 and 2.72 g cm^{-3} , which are higher than that of powder LCO (2.23 g cm^{-3}).

X-ray diffraction (XRD) analysis was conducted to confirm the structures of materials. As shown in Fig. 3, three Co_3O_4 samples match well with the standard pattern of Co_3O_4 (JCPDS Card No: 43-1003), and there are no other impurity peaks in the patterns. All-

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