



# Effect of calcination temperature on the morphology and electrochemical properties of $\text{Co}_3\text{O}_4$ for lithium-ion battery

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## ABSTRACT

A simple approach to synthesize  $\text{Co}_3\text{O}_4$  in mass production by using hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) as a precipitator via hydrothermal treatment has been developed. The samples were calcinated at different temperatures ranging from 300 to 600 °C and characterized by XRD and SEM. The structure became agglomerative and collapsed with an increase in calcination temperature. Evaluation of the electrochemical performance in combination with SEM and BET analysis suggests that there is an optimum calcination temperature for  $\text{Co}_3\text{O}_4$ . It is found that the retention capacity of well crystallized  $\text{Co}_3\text{O}_4$  hollow microspheres has a higher specific surface area at 300 °C and is almost above 94% after the 5th cycle at different current densities of 40 and 60  $\text{mA g}^{-1}$ , which shows good long-life stability and favorable electrochemical behaviors. Using EIS analysis, we demonstrated that lithium-ion conduction inside the SEI layers and charge transfer at the electrode/electrolyte interface became hindered with an increased calcination temperature, which was in good agreement with the electrochemical behaviors of three  $\text{Co}_3\text{O}_4$  electrodes. It is proposed that drastic capacity fading and the variation of resistive components (SEI layers and charge transfer) can be influenced by morphologies due to the calcination temperature.

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## 1. Introduction

Rechargeable Li-ion batteries have become the power source of choice for popular electronic equipment because of their high energy density. Interest in both the morphology and size control of synthesized materials has increased since the discovery of transition-metal oxides by Poizot et al. [1]. They suggested that the reactivity of the metal oxide particles is markedly determined by the morphology and size because the  $\text{Li}_2\text{O}$  formed during reduction is electrochemically inactive and the reverse removal of lithium is thermodynamically difficult. In addition, when reduced down to the nanometer scale, new properties such as chemical composition, relative size, and morphological structure are required due to the size effect. Therefore, attention has been dedicated to the study of the structure and electrochemical properties of such nano-scale or micro-sized transition-metal oxides.

As an important intrinsic p-type semiconductor, cobalt oxides belong to the family of transition-metal oxides and the most stable phase.  $\text{Co}_3\text{O}_4$ , with excellent cycle reversibility and high specific capacity, has received special interest over the last few years as one of the promising potential electrode materials for lithium-ion batteries [2]. Controlling fabrication of  $\text{Co}_3\text{O}_4$  materials with novel

morphology is of considerable interest. High temperature calcination is typically required to obtain good crystallinity of  $\text{Co}_3\text{O}_4$  in the manufacturing process. In this field, various synthetic routes of spinel oxide  $\text{Co}_3\text{O}_4$  have been proposed, such as surfactant-templated fabrication (180 °C) [3], a polyol process (500 °C) [4], solid-state formation (200–400 °C) [5], ultrasonic spray pyrolysis (300–900 °C) [6], and non-aqueous synthesis (350–750 °C) [7]. In addition, cobalt oxides with different morphologies have been synthesized, including nanowires/nanorods [8–10], nanowalls [11], nanoplatelets [12], nanotubes [13,14], and nanocubes [3,15–17].

Due to poor durability and rapid degradation on cycling, nano-structured hollow spheres and their related structures are attracting much attention due to their unique structural, electrical, and surface properties. It is well known that many fundamental properties and applications of materials depend not only on their shape and size, but also on their specific orientation and arrangement. The spherical particles are easy to close pack and have higher densities. They also have the favorable characteristics of reduced interface contact and better fluidity than the irregular particles [18,19]. In addition, the spherical texture is drastically altered with a transformation of the bulk crystallized initial particles into nanotextured particles made of nanodomains [20] and leads to its integrative surface modification to enhance its performance [21]. Furthermore, the uniform mesoporous structure with high surface area can be filled with electrolyte solution and enlarges the contact area for lithium ion pathways throughout the material. This facilitates higher activity for the lithium electrochemical reac-

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tion thereby shortening the diffusion length for lithium ions and improving the diffusion rate within the bulk of the prepared materials to achieve better performance. Presently, several synthetic and structural characterization reports of cobalt oxide spheres have been reported. For example, Jiang and Li [22] synthesized sphere-like  $\text{Co}_3\text{O}_4$  nanocrystals in ethylene glycol by a polyol method. Cao et al. [4] reported a polyol process to synthesize  $\text{Co}_3\text{O}_4$  with various shapes from nanoplates and microspherical composites. Oh et al. [6] synthesized  $\text{Co}_3\text{O}_4$  microspheres by using citric acid as a polymeric agent in combination with an ultrasonic spray pyrolysis method. Overall, obtaining high surface area  $\text{Co}_3\text{O}_4$  microsphere in large-scale production for high performance lithium-ion battery electrodes still remains a tremendous challenge.

Considering the advantages of a cost-effective and simplified preparation, the hydrothermal synthetic route would be of great interest. The hydrothermal method is applicable for the direct control of the particle microstructure, size, and composition. In this paper, we obtained  $\text{Co}_3\text{O}_4$  hollow microspheres with different crystallite sizes in mass production at various calcination temperatures by using hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) as the precipitator and trisodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) as the template. In order to investigate the effects of calcination temperature on the morphology and electrochemical properties of the  $\text{Co}_3\text{O}_4$ , we prepared three different temperatures ranging from 300 to 600 °C. Micrometer-sized  $\text{Co}_3\text{O}_4$  was obtained at an optimal temperature as Li-ion anode materials with the desired electrochemical behaviors.

## 2. Experimental

All the chemicals were of analytical purity and used as received. In a typical procedure, cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) and trisodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) were added to 60 mL of distilled water with stirring. The mole ratio of  $\text{Co}(\text{NO}_3)_2$ :HMT: $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  was 3:3:1. After stirring for 30 min, the solution was kept at 100 °C for 24 h in a Teflon-lined stainless steel autoclave. The precipitates were collected by centrifugation and washed with distilled water and absolute ethanol, and finally heated at 300, 450, and 600 °C for 3 h to obtain the desired products, named S-300, S-450, and S-600, respectively.

The phase purity of the product was characterized by X-ray power diffraction (Bruker D8 advance, Germany) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1518$  nm), employing a scanning rate  $10^\circ \text{min}^{-1}$  with  $2\theta$  ranging from 10 to 70°. The scanning electron microscopy (SEM) images were obtained using a Leo 1430 VP microscope. Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 instrument. Samples were degassed for 10 h under vacuum at 300 °C before measurement. The BET method was used to calculate the surface areas. The pore size distributions were derived from the adsorption branches of the Barrett–Joyner–Halenda (BJH) method.

The electrochemical properties of the powders were examined using a two-electrode electrochemical cell. The working electrode was prepared by a slurry coating. The slurry consisted of 80 wt.% active material, 15 wt.% acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone (NMP), and was spread on a nickel mesh current collector (diameter = 11 mm). The mesh was dried in a vacuum oven for 12 h at 100 °C. Test cells were assembled in an argon-filled glove box using Li foil as the counter electrode and polypropylene (PP) film as the separator. The electrolyte was 1 M  $\text{LiPF}_6$  in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Charge–discharge cycles of the half-cells were measured between 0.01 and 3.0 V versus  $\text{Li}/\text{Li}^+$  at various current densities of 20, 40 and  $60 \text{ mA g}^{-1}$  using a Land CT 2001 A battery program-control test system. The electrochemical impedance spectroscopy (EIS) of the electrode was performed

on a CHI 660B electrochemical workstation. The frequency of EIS ranged from 0.01 Hz to 100 kHz at the open circuit potential. Current density and specific capacity were calculated based on the mass of active material in the electrode. All electrochemical measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. Characterization of materials

Fig. 1 shows the XRD patterns of the  $\text{Co}_3\text{O}_4$  materials. Increasing the temperature led to a weakening of the diffraction peaks. It can be observed, however, that the positions of the characteristic peaks of three samples are consistent. No peaks for impurities were observed, indicating the high purity of the final products. Among the XRD patterns,  $\text{Co}_3\text{O}_4$  particles obtained at the calcination temperature of 300 °C are better crystallized with the strongest peak intensity (Fig. 1a). All the reflections can be indexed to the typical  $\text{Co}_3\text{O}_4$  phase with lattice constant  $a = 8.085$  Å (space group  $Fd\bar{3}m$  [227]), which agrees well with the standard crystallographic data (JCPDS card no. 78-1970). The pattern has three main diffraction peaks at 36.9, 65.2, and 31.2° ( $311$ ), ( $440$ ), and ( $220$ ) reflections, respectively.

The SEM images of three  $\text{Co}_3\text{O}_4$  materials are presented in Fig. 2. It can be seen that the morphologies of  $\text{Co}_3\text{O}_4$  materials are different. Increasing the calcination temperature increased the diameter of the  $\text{Co}_3\text{O}_4$  microspheres. The hollow microspheres were relatively monodisperse with a total thickness of approximately 2  $\mu\text{m}$  and the surface has the orderly sheet-like architecture when heated at 300 °C, as shown in Fig. 2a. When the calcination temperature was increased further, the particles became agglomerated. In addition, some of the microspheres were broken (Fig. 2b) and even more hollow architectures were collapsed (Fig. 2c). Furthermore, nanoflakes among the spheres are uniform at 300 °C. With the increase of the calcination temperature, nanoflakes increased and then collapsed. The results suggested that such induced crystallization and transformation can be affected by the calcination temperature in the present case.

Trisodium citrate is widely used for its dual functions as a chelate complex and stabilizing agent in nanocolloidal chemistry, which is rendered by the three carboxyl anions. These carboxyl anions can adsorb on the surface of metal ions and exert either hydrophobic or coulombic effects on metal ions, and thereby act as a template to form and stabilize the spherical structures [23]. With the effect of trisodium citrate, the inside layer gradually curved and filled the concave portion and the microsphere was formed, which

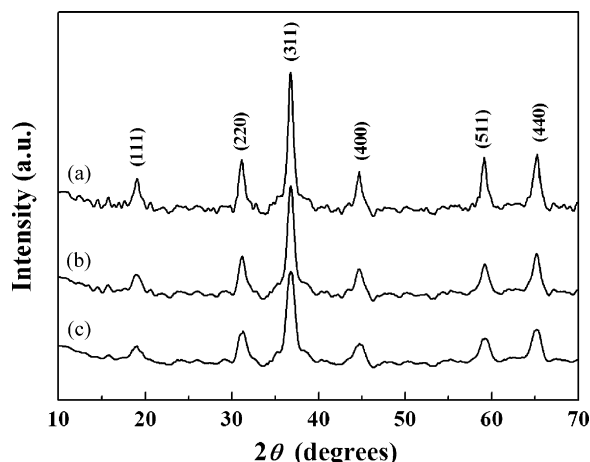


Fig. 1. XRD patterns of  $\text{Co}_3\text{O}_4$  materials: (a) S-300, (b) S-450, and (c) S-600.

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