Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 147 (2005) 264–268
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Non-aqueous synthesis of crystalline Co_3O_4 powders using alcohol and cobalt chloride as a versatile reaction system for controllable morphology

Z.W. Zhao *, Z.P. Guo, H.K. Liu

Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

Received 8 October 2004; accepted 19 January 2005
Available online 3 March 2005

Abstract

Crystalline Co_3O_4 powders with controllable morphology have been prepared using cobalt chloride and various alcohol precursors at different temperatures. The non-aqueous precursor is examined by simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA), and the obtained powders are characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). Co_3O_4 particles demonstrate a dramatic tetragonal dipyramid structure when synthesized from benzyl alcohol and cobalt chloride. A stable and reversible storage capacity for lithium of 740 mAh g^{-1} within 50 cycles is achieved on electrochemical performance testing.

Keywords: Cobalt oxide; Morphology; Non-aqueous synthesis, Lithium storage capacity, Battery, Fuel cell

1. Introduction

Cobalt oxides have a wide range of applications in various industrial fields. Among the various cobalt oxides, Co_3O_4 is an important ceramic oxide used for electrochemical, magnetic and catalytic applications. Poizot et al. [1] found that transition-metal oxides MO (M: Co, Ni, Cu, Fe) demonstrate high lithium storage capacity and good cycleability, so Co_3O_4 could serve as an anode material in place of the traditional carbon used in present lithium-ion batteries, Co_3O_4 also has considerable potential for use in metal–air batteries and fuel cells because it can catalyze the reduction of molecular oxygen to O^{2-} ions in an alkaline solution [2,3]. Various methods have been used to prepare Co_3O_4 particles, e.g., mechanochemical synthesis [4], polymer combustion route [5], gel hydrothermal oxidation [6], reduction–oxidation route [7], pulsed laser deposition [8], spray pyrolysis technique [9].

In recent years, the control of morphology has been a subject of concern in fabricating of semiconductor particles [10], magnetic particles [11], metal oxides [12,13], and metal sulfides [14,15]. This is because it is well known that many fundamental properties and applications of these materials depend not only on their shape and size, but also on their specific orientation and arrangement. Therefore, controlled fabrication of these materials to produce novel morphology is of considerable interest.

This work aims to prepare crystalline Co_3O_4 with controllable morphology from a non-aqueous precursor. The electrochemical performance of the Co_3O_4 as an anode material for lithium-ion batteries is systematically evaluated.

2. Experimental

Crystalline Co_3O_4 was prepared in a non-aqueous alcohol and cobalt chloride reaction system, by using ethanol, benzyl alcohol or hexyl alcohol. In a typical synthesis procedure, 400 mg of cobalt chloride was added to 20 mL of benzyl alcohol under vigorous stirring at room temperature. The vessel was then covered and the material was aged from a few days to several weeks at room temperature.

* Corresponding author. Tel.: +61 242 213 017; fax: +61 242 215 731.
E-mail address: zhengwei@uow.edu.au (Z.W. Zhao).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.01.021

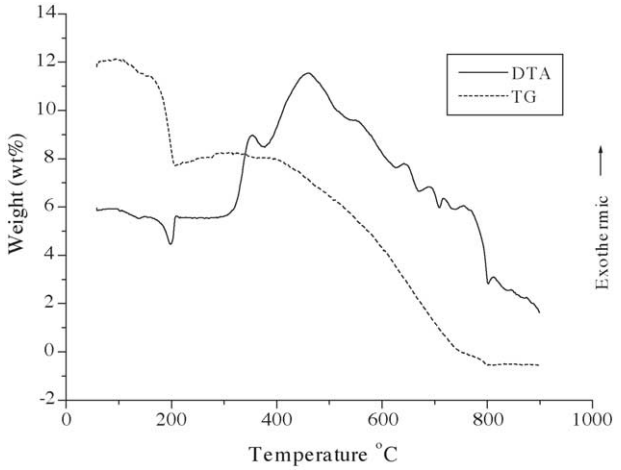

Fig. 1. DTA/TGA curves for pyrolysis precursor from cobalt chloride and benzyl alcohol mixture after ageing treatment.

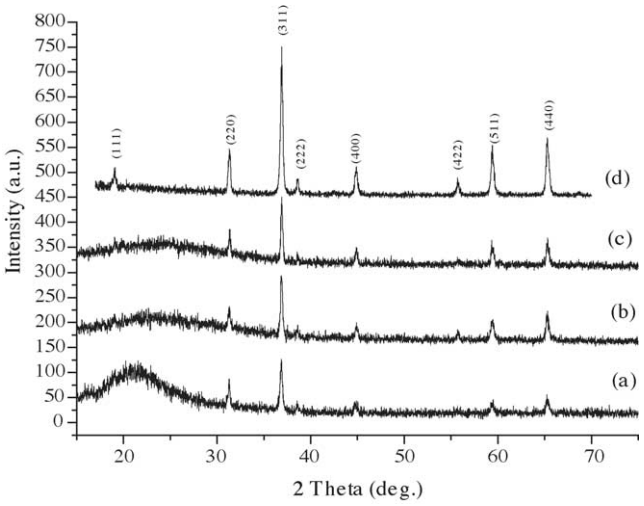

Fig. 2. XRD patterns for Co_3O_4 pyrolyzed from benzyl alcohol solvent at different temperatures: (a) 450 °C, (b) 600 °C, (c) 700 °C, (d) from hexyl alcohol solvent.

The mixture was next heated to 180 °C to obtain the pyrolysis precursor, and finally samples were heated to 450, 600 and 750 °C. When using ethanol and hexyl alcohol, the as-prepared powders were heated to 650 and 350 °C, respectively. All of the as-synthesized powders were highly crystalline. The as-prepared Co_3O_4 was characterized by X-ray diffraction (XRD; MO3xHF22, MacScience, Japan). The morphology of the Co_3O_4 was examined by scanning eletron microscopy (Leica/Cambridge Steroscan 440 Scanning Electron Microscope).

Coin cells were fabricated to evaluate the electrochemical properties of a Co_3O_4 anode in Li-ion cells. The Co_3O_4 electrodes were made by dispersing 72 wt.% active materials, 20 wt.% carbon black and 8 wt.% polyvinylidene fluoride (PVDF) binder in a dimethyl phthalate solvent to form a slurry, which was then spread on to a copper foil. The mass of each electrode was approximately 1 mg. The cells were assembled in an argon glove box (Mbraun, Unilab, USA). The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).

3. Results and discussion

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for the precursor prepared from cobalt chloride and benzyl alcohol solution are shown in Fig. 1. The broad peak located at about 180 °C is endothermic on the DTA curve and corresponds to a sample weight loss of six water molecules per formula unit, as deduced from the TGA curve. A much broader exothermic peak is observed after 300 °C and is indicative of the decomposition reaction of cobalt chloride and the composition reaction of cobalt oxides. It accompanies a weight loss on the TGA curve.

The XRD patterns for the samples obtained under different conditions are shown in Fig. 2. All the peaks can be indexed to the Co_3O_4 powders. When the precursor was pyrolyzed above 300 °C, black powders were obtained. Treatment at higher temperatures results in slightly sharper diffraction peaks.

Scanning electron micrographs of the benzyl alcohol precursor after the solution was heat-treated at 180 °C are shown in Fig. 3 and those for Co_3O_4 powders prepared at different temperatures (450–750 °C) from benzyl alcohol solvent are given in Fig. 4. The morphology of the materials is regular and polyhedral with tetragonal dipyramid structures. The degree of agglomeration of the particles increases with increasing temperature. Primary crystals of the agglomerates are visible in the micrographs.

Micrographs of the Co_3O_4 powders prepared in ethanol and hexyl alcohol solution are presented in Fig. 5. These powders have an irregular morphology. Therefore, it is clear that the morphology of as-prepared Co_3O_4 powders depends mainly on the choice of solvent. In different solvents, before the pyrolysis treatment, the cobalt species and

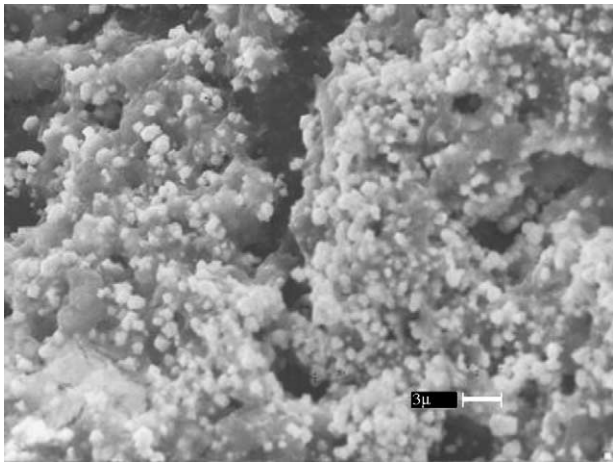

Fig. 3. Electron micrograph of benzyl alcohol solvent precursor after heat treatment at 180 °C.