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

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.
© 2005 Elsevier B.V. All rights reserved.

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.
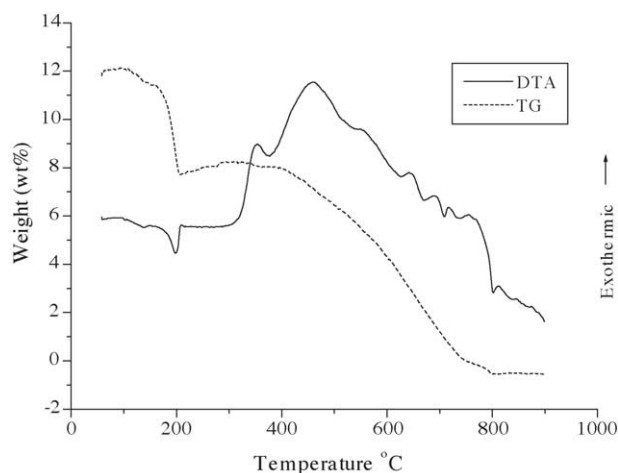 *E-mail address:* zhengwei@uow.edu.au (Z.W. Zhao).

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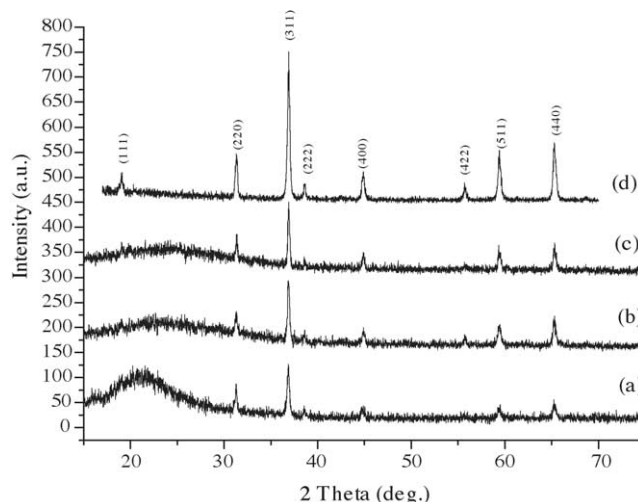

Fig. 2. XRD patterns for Co_3O_4 pyrolyzed from benzyl alcohol solvent at different temperatures: (a) 450 °C, (b) 600 °C, (c) 700 °C, (d) from hexyl alcohol solvent.

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
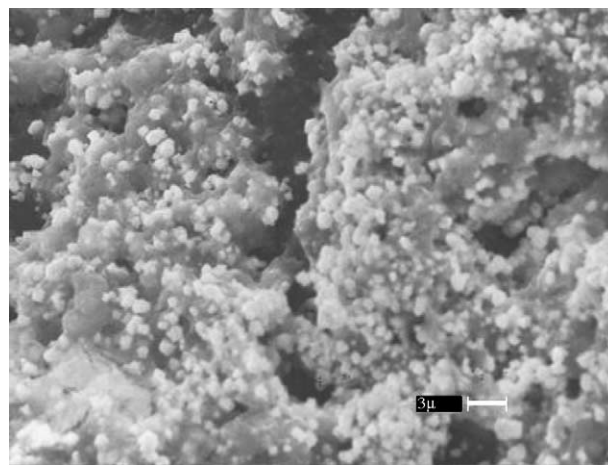

Fig. 3. Electron micrograph of benzyl alcohol solvent precursor after heat treatment at 180 °C.
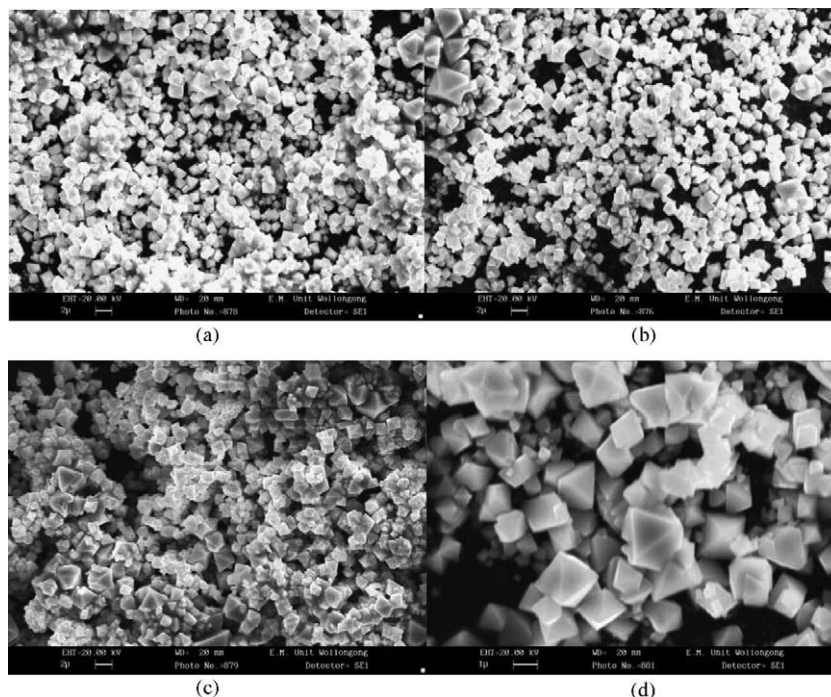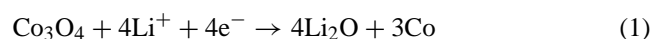
Fig. 4. Electron micrographs of crystalline Co_3O_4 pyrolyzed from benzyl alcohol solvent at different temperatures: (a) 450 °C, (b) 600 °C, (c) 700 °C, (d) large image of (c).

their environment in the reactor are different. The nucleation and growth of Co_3O_4 crystals are related to the initial cobalt species and solvent with the result that they affect the morphology of the as-formed Co_3O_4 powders. Benzyl alcohol in this non-aqueous reaction system definitely contributes to the nucleation and growth of polyhedral Co_3O_4 crystals.

The electrochemical properties of cobalt oxides as anode materials in Li-ion cells were evaluated via charge–discharge cycling tests. The cycling was performed over a voltage range of 0.01–3.0 V versus a Li/Li$^+$ counter electrode. The initial two discharge–charge curves for the Co_3O_4 sample synthesized from benzyl alcohol solvent are shown in Fig. 6. During the first discharge, the potential falls rapidly to reach a large plateau at 1.0 V, and then slowly drops to 0.01 V. The charge potential commences a plateau at about 2.0 V. The discharge capacity of lithium ions on the first discharge reaches

1104 mAh g^{-1}, and the subsequent charge capacity amounts to 798 mAh g^{-1}. The discharge capacity on the second cycle is about 796 mAh g^{-1}, and the second charge capacity is 762 mAh g^{-1}. Charge–discharge tests of coin cells were performed for 50 cycles. After 50 cycles, the capacity remains around 740 mAh g^{-1}, and a large plateau continues through to the end of 50 cycles (Fig. 6).

The reaction mechanism of cobalt oxide with lithium in Li-ion cells is proposed to be a displacive redox reaction:

$$Co_3O_4 + 4Li^+ + 4e^- \rightarrow 4Li_2O + 3Co \tag{1}$$

$$4Li \leftarrow 4Li^+ + 4e^- \tag{2}$$

$$Co_3O_4 + 8Li \rightleftarrows 4Li_2O + 3Co \tag{3}$$

The reaction of lithium ions with cobalt oxide forming lithium oxide and cobalt is thermodynamically feasible.
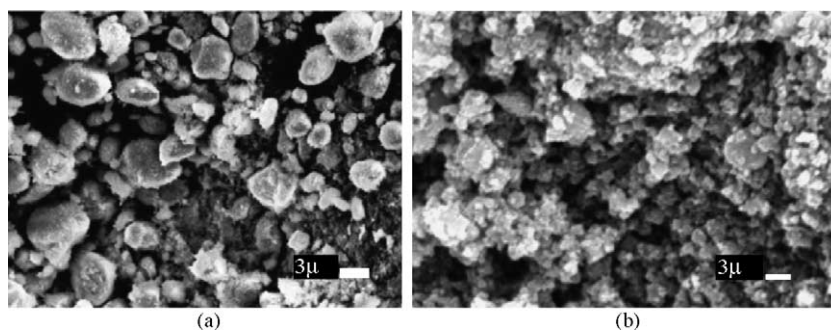

Fig. 5. Electron micrographs of crystalline Co_3O_4 pyrolyzed from (a) ethanol solvent, (b) hexyl alcohol solvent.
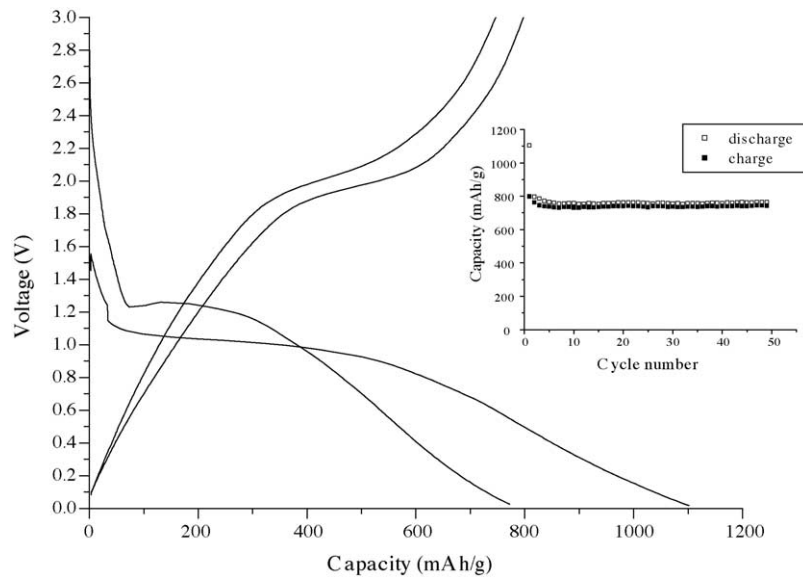
Fig. 6. First two charge–discharge curves of as-synthesized Co_3O_4 pyrolyzed from benzyl alcohol solvent in Li-ion test cell.

Nevertheless, Li_2O is believed to be electrochemically inactive [1].

During the first discharge, a solid electrolyte interphase (SEI) layer appears around the initial Co_3O_4 particle, and this will lead to an irreversible capacity loss of the Co_3O_4 anode material. From cyclic voltammetry (CV) measurements, there are two reduction peaks at around 1.2 and 0.9 V, and one oxidation peak at 2.0 V during the redox reaction in the first cycle (Fig. 7). The high voltage reduction peak on the CV curve is attributed to the formation of the SEI layer. In the subsequent scanning cycles, there is only one pair of redox peaks on the CV curves. The reduction peaks move to 1.1 V, and the oxidation peaks remain at 2.0 V.

The as-prepared Co_3O_4 powders from different solvents were examined via charge–discharge cycling. All of them ex-
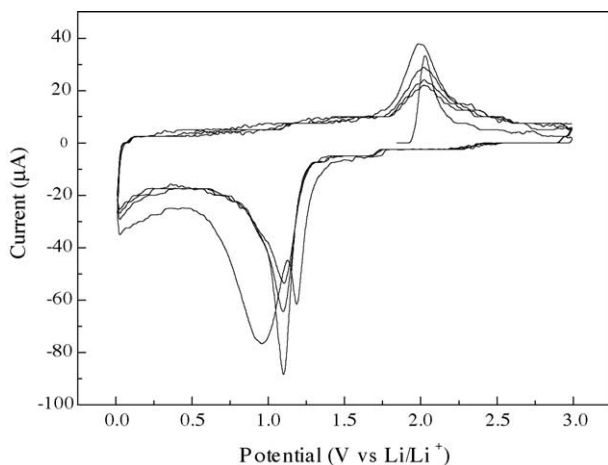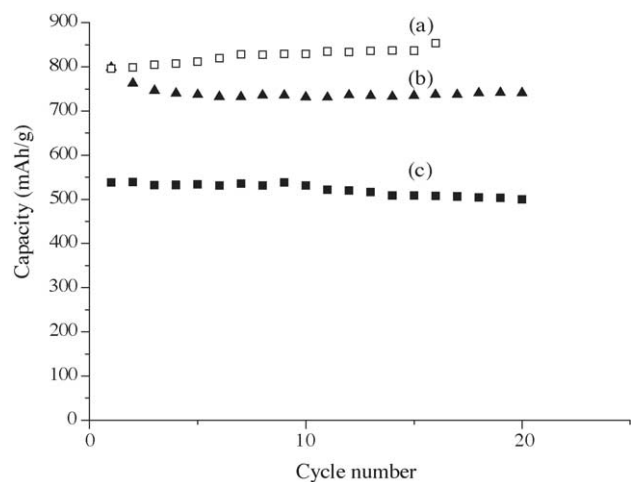

Fig. 8. Cycleability of Co_3O_4 powders pyrolyzed from (a) ethanol solvent, (b) benzyl alcohol solvent, (c) hexyl alcohol solvent.

hibited promising cycle-life as anodes in Li-ion cells (Fig. 8). The capacity increases slightly during cycling.

4. Conclusion

This study illustrates the successful synthesis of high-quality crystalline Co_3O_4 powders with visible tetragonal dipyramid structures via a versatile non-aqueous reaction system using benzyl alcohol solvent. The reaction between cobalt oxide and alcohol leads to polyhedral particle shapes; the morphology is controlled by selection of the solvent. The process is simple, allows for scale-up, and leads to highly crystalline particles with controllable morphology. The as-synthesized Co_3O_4 demonstrates high lithium storage

Fig. 7. Cyclic voltammograms of as-synthesized Co_3O_4 pyrolyzed from benzyl alcohol solvent in Li-ion test cell.

capacity and promising cycle-life as an electrode material for Li-ion batteries.

Acknowledgements

References

[1] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarason, Nature 407 (2000) 496.

[2] U. Morales, A. Campero, O. Solorza-Feria, J. New Mater. Electrochem. Syst. 2 (1999) 89.

[3] J.P. Singh, R.N. Singh, J. New Mater. Electrochem. Syst. 3 (2000) 137.

[4] H. Yang, Y. Hu, X. Zhang, G. Qiu, Mater. Lett. 58 (2004) 378.

[5] J. Jiu, Y. Ge, X. Li, L. Nie, Mater. Lett. 54 (2002) 260.

[6] Y. Jiang, Y. Wu, B. Xie, Y. Xie, Y. Qian, Mater. Chem. Phys. 74 (2002) 234.

[7] Y. Ni, X. Ge, Z. Zhang, H. Liu, Z. Zhu, Q. Ye, Mater. Res. Bull. 36 (2001) 2383.

[8] N. Koshizaki, A. Narazaki, T. Sasaki, Scr. Mater. 44 (2001) 1925.

[9] E. Fujii, H. Torii, A. Tomozawa, R. Takayama, T. Hirao, J. Mater. Sci. 30 (1995) 6013.

[10] H. Xu, H. Wang, Y. Zhang, W. He, M. Zhu, B. Wang, H. Yan, Ceram. Int. 30 (2004) 93.

[11] C.Y. Wang, G.M. Zhu, Z.Y. Chen, Z.G. Lin, Mater. Res. Bull. 37 (2002) 2525.

[12] I.W. Lenggoro, Y. Itoh, N. Iida, K. Okuyama, Mater. Res. Bull. 38 (2003) 1819.

[13] C.Y. Wang, G.M. Zhu, S.L. Zhao, Z.Y. Chen, Z.G. Lin, Mater. Res. Bull. 36 (2001) 2333.

[14] H. Hu, B. Yang, J. Zeng, Y. Qian, Mater. Chem. Phys. 86 (2004) 233.

[15] P. Zhang, L. Gao, J. Colloid Interface Sci. 272 (2004) 99.