Electrochimica Acta 56 (2011) 4876–4881

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Molten hydroxides synthesis of hierarchical cobalt oxide nanostructure and its application as anode material for lithium ion batteries

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ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form 24 February 2011
Accepted 4 March 2011
Available online 17 March 2011

Keywords:
Cobalt oxide
Nanostructure
Anode
Lithium ion battery

ABSTRACT

Hierarchical Co_3O_4 nanostructure is synthesized via a self-assembled process in molten hydroxides. The morphologies, crystal structures and the phase transformation processes are analyzed by field-emission scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. As an anode material for lithium ion batteries, the hierarchical Co_3O_4 exhibit an initial capacity of 1336 mAh g^{-1} and a stable capacity of 680 mAh g^{-1} over 50 cycles. More importantly, high rate capability is obtained at different current densities between 140 and 1120 mA g^{-1}. The improved electrochemical performance of Co_3O_4 could be attributed to the unique hierarchical nanostructure.

1. Introduction

Cobalt oxide (Co_3O_4) has attracted increasing attention due to its unique properties and potential applications in diverse fields, such as catalysis, gas sensors and field-emission devices [1–4]. In addition, Co_3O_4 is also regarded as a promising alternative anode material for rechargeable lithium ion batteries [5], which exhibits a high theoretical capacity of 890 mAh g^{-1}. However, the severe volume expansion/contraction associated with Li^+ insertion and extraction processes causes the pulverization of electrode and leads to a rapid deterioration in capacity [6,7]. To overcome this intrinsical drawback, it is suggested that hybridizing Co_3O_4 with carbon material is an effective approach [8,9]. Nevertheless, this strategy sacrifices the capacity of Co_3O_4 due to the introduction of carbon. Moreover, the reliable synthesis of well-designed Co_3O_4/carbon nanocomposites remains a challenge. In general, it is well accepted that the morphology of Co_3O_4 nanostructures can greatly affect their electrochemical properties [10,11]. Over the past few years, intensive researches have been devoted to the synthesis of novel Co_3O_4 nanostructures, which reveals a promising way to improve the electrochemical performances of Co_3O_4 anodes. For instance, various Co_3O_4 nanostructures such as nanotubes [12,13], octahedral cages [14], mesoporous needles [15], hollow structures [16,17] and pompon-like microspheres [18] have been reported and exhibit the enhanced electrochemical properties. However, there should be still much space for progress to achieve the satisfactory cycle performance and high rate capability for the practical application of Co_3O_4 anodes, particularly in terms of novel morphology and controlled synthesis. In particular, hierarchical architectures assembled by low-dimensional building blocks have been considered to be the ideal nanostructures for enhanced electrochemical performances [19–21]. The improved properties could be mainly attributed to the loose structure, large surface area, and shortened Li^+ diffusion distance.

The molten-salt synthesis method is one of the simple, versatile, and cost-effective approaches for obtaining oxide nanostructures [22]. Recently, Wang and co-workers demonstrated the feasibility of a composite-hydroxide-mediated (CHM) approach to synthesize oxide nanostructures [23]. This method is based on the reactions of raw materials in eutectic hydroxide melts and it provides a one-step, convenient, low cost, nontoxic and mass-production route for various oxide nanostructures. Up to now, a wide range of complex oxides, hydroxides and simple oxides has been synthesized by CHM approach, including $BaTiO_3$, $CoFe_2O_4$, $Pb_2V_2O_7$, Niobate, $La(OH)_3$, CuO, CeO_2, etc. [24–28]. However, to the best of our knowledge, there is few works to report the synthesis of Co_3O_4 nanostructures via CHM approach.

Herein, we adopt the so-called CHM approach to synthesize hierarchical Co_3O_4 nanostructures. It is found that the as-obtained Co_3O_4 nanostructure is assembled by extremely thin nanosheets. The reaction mechanism for the formation of Co_3O_4 nanostructure in molten hydroxides is discussed. Motivated by the unique morphology, the electrochemical properties of the Co_3O_4 nanostructure are investigated. In addition, the effect of the annealing temperature on the electrochemical performance is also presented.

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doi:10.1016/j.electacta.2011.03.027

As anode material for lithium ion batteries, the hierarchical Co_3O_4 nanostructure displays superior lithium storage properties with good cycle stability and high rate capability.

2. Experimental

In a typical experiment, a teflon vessel filled with 20 g mixed hydroxides (NaOH:KOH = 51.5:48.5) was putted in a furnace and then heated up to 200 °C. When the hydroxides melted, 0.476 g $CoCl_2{\cdot}6H_2O$ was added and the mixture was stirred until a uniform suspension was obtained. It is found that the black precipitates were formed immediately. After maintaining at 200 °C for a period of time, the vessel was taken out and cooled to room temperature naturally. Then, deionized water was added to dissolve the residual hydroxides. The precipitates were harvested by centrifugation and washed thoroughly with deionized water and ethanol. Finally, Co_3O_4 samples were obtained by calcining the black precursors at 500 °C for 6 h. The heating rate was below 1 °C/min.

The structure, morphology of the products were characterized with X-ray powder diffraction (XRD, Bruke D8-Advance, Cu-Kα, λ = 0.15406 nm), field-emission scanning electron microscope (FESEM, JEOL JSM-7100F) and transmission electron microscopy (TEM, JEOL JEM-2100). The N_2 adsorption and desorption isotherm was obtained at 77 K using Physisorption Analyzer (ASAP 2020). The BET surface area was estimated using adsorption data in a relative pressure ranging from 0.06 to 0.3.

Electrochemical performance of the hierarchical Co_3O_4 nanostructure was investigated with two-electrode Swagelok cells. For working electrodes, the Co_3O_4 samples mixed with carbon black and polyvinylidene fluoride (PVDF) at a mass ratio of 70:20:10 were dispersed in N-methyl pyrrolidinone (NMP). Then, the slurry was coated uniformly onto copper foils (Φ = 10 mm) and dried in vacuum at 100 °C for 12 h. Test cells were assembled in argon filled glove box. Metallic lithium foil was used as counter electrode. The electrolyte was made by dissolving 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) with the volume ratio of 1:1. Galvanostatical charge and discharge tests were carried out on a battery testing system (Arbin-BT2000) with the voltage range of 0.01–3.0 V (vs. Li/Li^+). Cyclic voltammograms were performed on Ametek VMC-4 electrochemical testing system between 3.0 V and 0 V at a scan rate of 0.5 mV s^{-1}.

3. Results and discussion

In this work, the mixed hydroxides are employed not only as the solvent but also as the reactant for preparing the precursors. Fig. 1a–d displays the morphological images of the precursors, which are obtained with a reaction time of 1 min (precursor A)

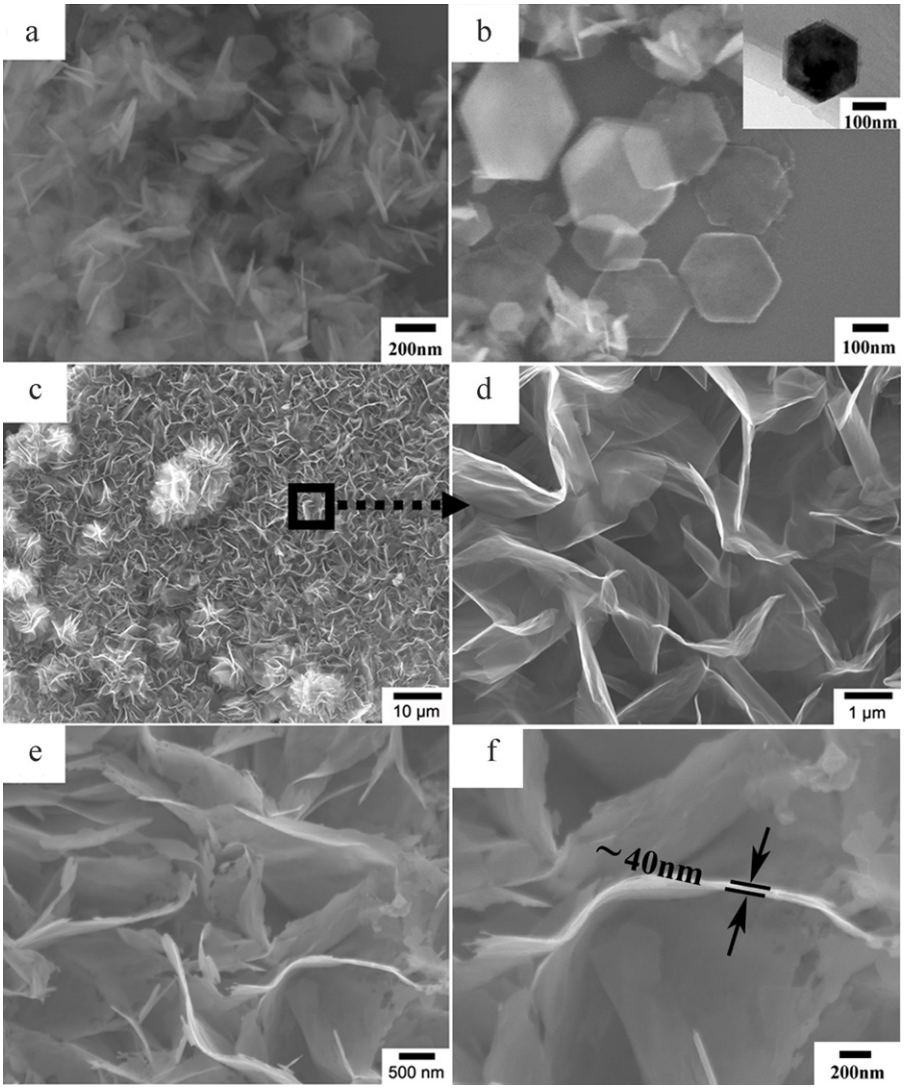

Fig. 1. Morphological images of as-synthesized precursors with a reaction time of (a and b) 1 min (precursor A), (c and d) 8 h (precursor B) and (e and f) SEM image of Co_3O_4 nanostructure produced by calcining the precursors B at 500 °C for 6 h.