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Microwave- or conventional–hydrothermal synthesis of Co-based materials for electrochemical energy storage

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Abstract

Crystalline Co_3O_4 and $Co(OH)_2$ were synthesized using $Co(NO_3)_2$ as a precursor by conventional–hydrothermal and microwave–hydrothermal routes, respectively. The Co_3O_4 phase showed cubic morphologies while the β-$Co(OH)_2$ phase exhibited plate-like shapes. The electrochemical performances of Co_3O_4 and $Co(OH)_2$ phases were evaluated as electrode materials for lithium-ion battery anodes, cathodes and supercapacitors. Both Co_3O_4 and $Co(OH)_2$ phases showed pseudocapacitive performances in Li_2SO_4 and KOH electrolytes. The Co_3O_4 and $Co(OH)_2$ phases were found to be more promising as anodes than as cathodes in lithium-ion batteries. The $Co(OH)_2$ electrodes showed higher specific capacitances than those of Co_3O_4 materials.

Keywords: Co_3O_4; $Co(OH)_2$; Lithium-ion battery; Anode; Cathode

1. Introduction

Batteries and electrochemical capacitors have become hot topics in the fields of chemistry, materials science and electrochemistry [1–3], because electrical energy storage to operate electronic devices has become extremely important at present. With many decades of world-wide research, advances in reaction mechanisms, electrode materials and their performances have been made [4–6]. However, further advances are needed in battery research to meet some higher performance requirements such as larger capacity, longer cycling life, and better rate performances [1]. Superior electrodes could be prepared using micro-/nanomaterials with controllable morphologies and sizes because crystal size and morphology play an important role in the chemical and physical properties [7–9]. However, it remains a great challenge to develop a simple, low-cost and environmentally friendly method for the one-pot synthesis of micro-/nanomaterials with specific crystal structures and morphologies. Recently, various electrode materials such as CuO, Cu_2O, Co_3O_4 and MnO_2, have been synthesized by low temperature routes to study their electrochemical performances [10–14]. Microwave–hydrothermal (M–H) route showed clear advantages such as shorter reaction time and well-crystallized phases of different morphologies compared to that of the conventional–hydrothermal (C–H) method. Therefore, the microwave–hydrothermally synthesized phases have been employed to fabricate electrode materials for lithium-ion batteries and supercapacitors, which could show the relationship of phase to its electrochemical performance [15–17]. More recently, novel water-soluble pseudocapacitors with ultrahigh specific capacitances were reported where commercial inorganic salts were directly used

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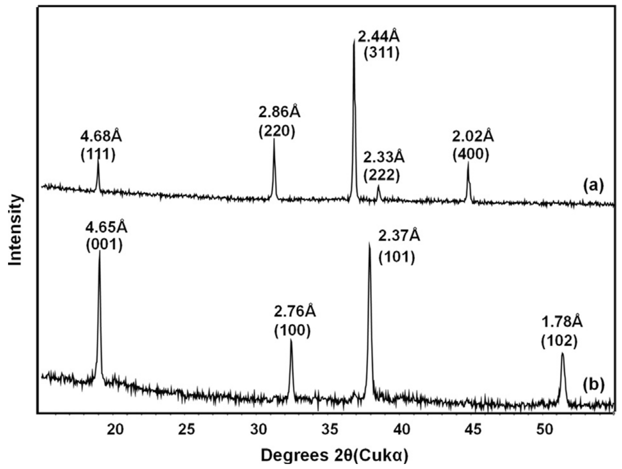

Fig. 1. Powder XRD patterns of Co_3O_4 (matched to JCPDS 42-1467) prepared by the conventional–hydrothermal process at 200 °C for 5 days (a) and $Co(OH)_2$ (matched to JCPDS 30-0443) by the microwave–hydrothermal process at 140 °C for 2 h (b).

as electrode materials [18–20]. For example, pseudocapacitors made from water-soluble $CoCl_2$ salts have delivered very high specific pseudocapacitances of ~1962 F/g [20].

Co-based micro-/nanomaterials, such as Co_3O_4, and $Co(OH)_2$, have been previously synthesized using different methods [21–23]. Co-based micro-/nanomaterials with various morphologies have shown specific chemical and physical properties with many applications in catalysts, adsorbents, high-performance electrochemical materials of lithium-ion batteries and supercapacitors [14,24,25]. Herein, we used conventional–hydrothermal and microwave–hydrothermal routes to synthesize Co_3O_4 and $Co(OH)_2$ electrode materials, respectively. The crystalline phases and their morphologies were characterized by XRD and SEM, respectively. The electrochemical performances of the above two phases were evaluated to test their potential application in lithium-ion batteries and supercapacitors.

2. Experimental

2.1. Synthesis

Co_3O_4 and $Co(OH)_2$ were synthesized by using analytical grade $Co(NO_3)_2$ from Aldrich. For Co_3O_4 synthesis, first $Co(NO_3)_2$ was adjusted to pH of 8.5 with 3 M NH_4OH and then treated by conventional–hydrothermal route at 200 °C for 5d. For $Co(OH)_2$ synthesis, first 5 g Co nitrate was dissolved in 65 ml of water and pH was adjusted to 8.5 by 3 M NH_4OH followed by treatment under microwave–hydrothermal conditions at 140 °C for 2 h.

2.2. Characterization

The prepared Co-based materials were characterized by powder X-ray diffraction (XRD) for phase detection. Powder XRD patterns were obtained on a PANalytical X'Pert MPD diffractometer operated at 45 kV voltage and 40 mA current with a PIXcel detector and using Cu Kα radiation. Field-emission scanning electron microscope (FESEM, Hitachi-S4800) was used to determine the particle size and shape of synthesized materials.

2.3. Testing for lithium-ion batteries

The working electrodes were prepared by mixing each active material, acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10. The mixtures were slurried with N-methyl-2-pyrrolidone, and pasted onto copper foils as anodes and onto aluminum foils as cathodes. For the electrochemical properties, coin cells (CR2025) were fabricated using lithium metal as the counter electrode. 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 vol%) served as the electrolyte. A galvanostatic cycling test of the assembled half-cells was conducted on a LAND CT2001A system.

2.4. Testing for supercapacitors

Working electrodes were prepared by mixing each sample, acetylene black, and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10. The resulting paste was pressed on a sheet of porous nickel foam at 10 MPa. All experiments were performed in a three-electrode open beaker cell in 1 M Li_2SO_4 and 2 M KOH electrolytes. The saturated calomel electrode (SCE) served as the reference electrode, and the Pt wire as a counter electrode. The cyclic voltammetry (CV), and galvanostatic charge–discharge measurements were carried out by an electrochemical workstation (CHI 660D).

3. Results and discussion

Crystalline $Co(OH)_2$ and Co_3O_4 samples were synthesized (Fig. 1) by microwave–hydrothermal and conventional–hydrothermal routes, respectively, using $Co(NO_3)_2$ as starting precursor at different reaction temperatures. The reactions for the synthesis of $Co(OH)_2$ and Co_3O_4 are as follows:

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \tag{1}$$

$$6Co(OH)_2 + O_2 \rightarrow 2Co_3O_4 + 6H_2O \tag{2}$$

Amorphous $Co(OH)_2$ products were first formed in the alkaline pH. Then, $Co(OH)_2$ was crystallized at 140 °C for 2 h by using microwave–hydrothermal route. When the reaction temperature was increased to 200 °C, additional oxidation of Co^{2+} occurred and led to the crystallization of Co_3O_4 under the conventional–hydrothermal conditions. Due to the weak oxidation ability of O_2, the crystallization of Co_3O_4 needed a much longer reaction time of 5 days.

Fig. 1 shows the X-ray diffraction patterns of Co_3O_4 and $Co(OH)_2$. Pure single phases of $Co(OH)_2$ and Co_3O_4 were obtained with no detectable impurities. All the diffraction peaks in Fig. 1a were indexed to pure cubic phase of Co_3O_4 according to JCPDS 42-1467 (cubic phase) and all the diffraction peaks in Fig. 1b were indexed to pure hexagonal