



Flower-like porous cobalt(II) monoxide nanostructures as anode material for Li-ion batteries☆



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ABSTRACT

In the present study, a microwave-assisted, solution-based route has been employed to obtain porous CoO nanostructures. Detailed characterization reveals that the flower-like nanostructures comprise petal-like sheets, each of which is made of an ordered, porous arrangement of crystallites of CoO measuring about 6 nm. TEM analysis shows that each “petal” is an oriented aggregate of CoO nanocrystals, such aggregation promoted by the hydroxyl moieties derived from the solution. The structure provides a large specific area as well as the porosity desirable in electrodes in Li-ion batteries. Electrochemical measurements carried out on electrodes made of nanostructured CoO show excellent Li ion-storing capability. A specific capacitance of 779 mAh g⁻¹ has been measured at a specific current of 100 mA g⁻¹. Measurements show also excellent cyclability and coulombic efficiency. Impedance spectroscopy provides evidence for charge transfer occurring in the porous networks.

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1. Introduction

Rechargeable batteries are regarded as the best choice for powering portable electronic devices. Li-ion batteries (LIBs) are especially attractive because they have a storage capability per unit weight and volume which is 100–150% greater than that of more traditional aqueous batteries. Since their commercialization in the early 1990s, a dramatic growth in the research and development efforts on LIBs as well as in their practical use has taken place. From consumer electronics to medical devices, LIBs have proven to be the stand-alone power supplies of choice [1–4]. However, they still present various problems, such as a large volume change due to the reactions involved, safety hazards, and a relatively high cost. The development of new materials and routes to integrate them into LIBs as electrodes has therefore been pursued and remains a challenge.

At present, commercialized carbon-based anode materials - in particular, graphite-related nano-carbons - exhibit superior cycle performance in LIBs. However, due to their low specific capacity, they cannot satisfy the demand for high-energy-density batteries [5]. So, much effort is being made to develop new anode materials with higher capacity to replace the carbon-based materials. Various electrode

materials, e.g., oxides, sulfides, carbonaceous oxide composites, and core-shell nanostructures have been developed both for the cathode and the anode in LIBs [6–9].

Oxides of Co, Sn and Ti, sulfides of Fe, V, and their carbonaceous composites, are some of the electrode materials for LIBs investigated to date [10–13]. In particular, cobalt oxides, Co₃O₄ and CoO, are both promising electrode materials because of their high theoretical specific capacity (890 mAh g⁻¹ and 715 mAh g⁻¹, respectively). Owing to its unique electrochemical performance, CoO, in particular, has been investigated by several research groups as anode material for LIBs [14–16]. However, synthesis of phase-pure CoO is difficult because of the greater thermodynamic stability of Co₃O₄ and the ready reducibility of CoO to Co metal. Numerous methods have been employed to synthesize phase-pure CoO including thermal decomposition of cobalt complexes, and the micro-emulsion, solvothermal, molten salt, and microwave routes [17–21]. Among these, the microwave-assisted chemical route is attractive because of its speed, the concomitant energy efficiency, and cost-effectiveness [22].

Though non-carbonaceous materials show high specific capacity, their use as electrode materials in LIBs is limited by their poor ionic/electronic conductivity, capacity-fading and poor rate performance. Characteristics of efficient electrodes includes material with higher specific surface area and porosity. Nanostructured materials have numerous advantages over conventional micron-scale electrode materials, as they can accommodate strain caused by volume expansion during cycling, without pulverization or capacity fading [23]. The microwave-assisted route has been shown to produce well-controlled particle size and microstructure in the resulting material [24,25]. In microwave-

☆ Electronic supplementary information (ESI) is available on the TEM analysis of the electrode after charge–discharge cycles and on impedance measurements at different potentials.

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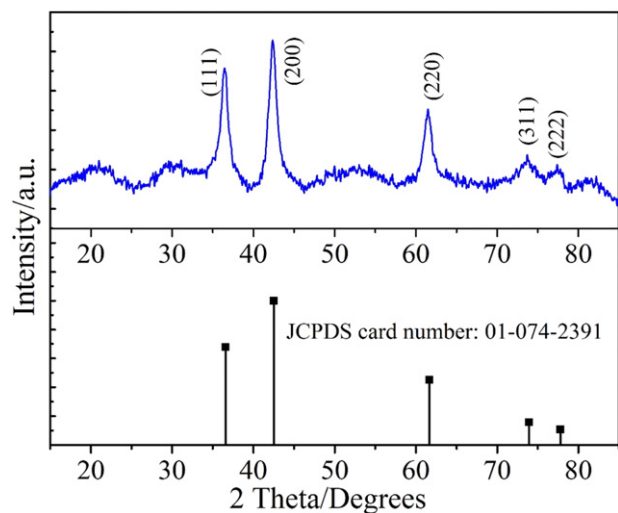


Fig. 1. XRD pattern of the powder obtained by microwave route showing well crystallized phase pure CoO

assisted synthesis, these characteristics can be controlled through various parameters, including the choice of reactants and solvent, microwave power, and the duration of microwave irradiation [26].

We report here on the microwave-assisted synthesis of CoO with a unique, flower-like, porous nanostructure. Detailed characterization affirms the phase purity of the oxide and the oriented aggregation of nanometric grains in each “petal”. CoO with such nanostructure has been employed as the anode material to measure its ability to store Li ions. From these measurements, a discharge capacity of 779 mAh g^{-1} has been calculated. The kinetics of the electrode process at the interfaces has also been studied by electrochemical impedance measurements.

2. Experimental procedure

2.1. Synthesis and characterization of CoO

Co(II) acetylacetonate dihydrate was synthesized in laboratory and was used as precursor to phase-pure CoO. Briefly, about 0.85 g of the complex was added to 10 ml of benzyl alcohol, followed by the addition of a solution of 0.3 g polyvinylpyrrolidone (PVP, K-90, mol. wt. 360,000) in 10 ml of water. The mixture was stirred for 30 min in a 250 ml round-bottomed flask connected externally to a water condenser, and then subjected to microwave irradiation (2.45 GHz) for ten minutes in a “domestic” microwave oven, applying 900 W of power. The suspension obtained from this process was centrifuged and the resulting powder material dried. The final product was obtained by annealing the powder at 400°C for one hour under flowing ultra-high purity nitrogen.

The crystallinity of the powder obtained by the microwave route was examined by X-ray powder diffraction (PANalytical instrument, $\text{Cu-K}\alpha$ radiation). Morphological analysis of the powder was carried out by electron microscopy (FESEM-Zeiss Ultra-55 and FE-TEM Technai F-30). Nitrogen adsorption/desorption experiments were carried out at 77 K (Micromeritics surface area analyser model ASAP 2020) to determine the specific surface area and porosity of the sample. The specific surface area was calculated in the p/p^0 range of 0.05–0.25 by the Brunauer-Emmett-Teller (BET) method using multiple points of adsorption isotherm, and pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms. Core-level X-ray photoelectron (XPS) spectra of the synthesized powder were gathered on a Thermo Scientific Multilab-2000 instrument, with monochromatized $\text{Mg-K}\alpha$ radiation. The active mass of the electrode material, i.e., cobalt oxide, coated on Cu foils for

electrochemical measurements was determined using a semi-micro balance (Mettler AE240, resolution $10 \mu\text{g}$).

2.2. Assembling the electrochemical cells

The electrodes for the electrochemical cell were prepared by adding 70% by weight of the CoO powder (obtained from microwave synthesis) to 20% acetylene black and 10% polyvinylidene difluoride. Slurry was made of the above mixture by adding a few drops of N-methylpyrrolidone, and the slurry was coated onto a 0.25 mm-thick Cu foil of 12 mm diameter. The foil was then dried overnight at 60°C . Cell construction and sealing were carried out in an argon-filled glove box (MBraun Model Unilab) using an air-tight glass container. The electrochemical “Swagelok cells” were assembled using lithium foil (Aldrich) for both the counter and reference electrodes, with the CoO film on Cu foil as the working electrode. An adsorbent glass mat (AGM) was used as the separator between the electrode material and the Li foil. The electrolyte employed was 1 M LiPF_6 dissolved in ethylene carbonate, diethyl carbonate, and dimethyl carbonate (2:1:2 v/v), each of which was used as received from Chameleon.

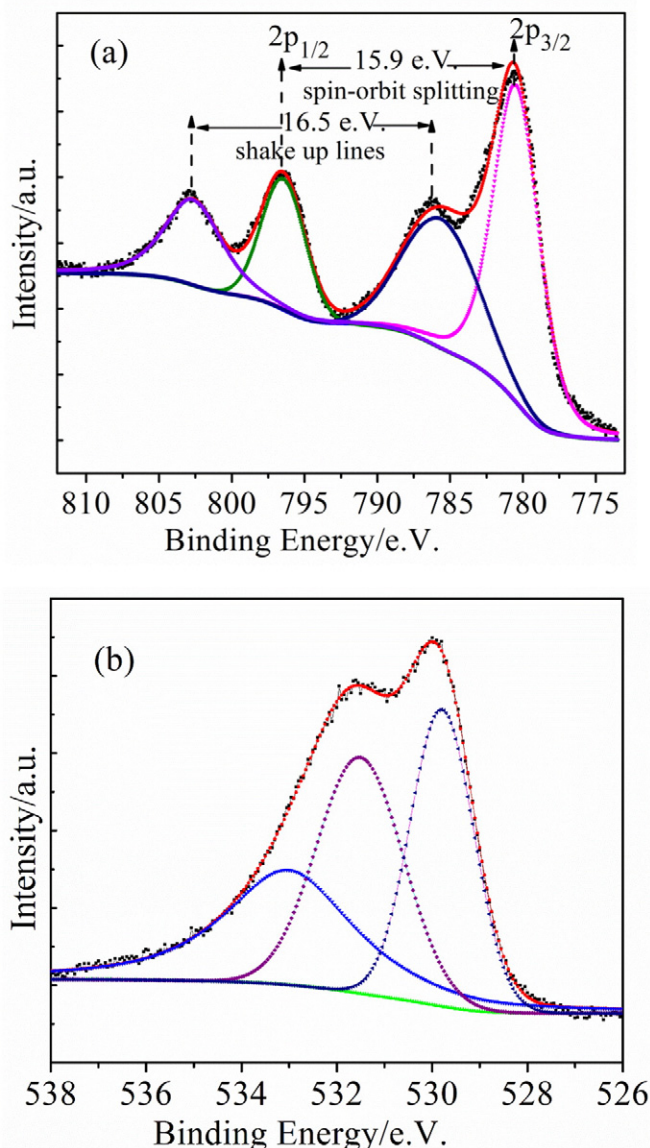


Fig. 2. XPS spectrum of phase pure CoO (a) Deconvoluted Co 2p (b) Deconvoluted O 1 s.

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