Contents lists available at ScienceDirect

Ceramics International

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

Syntheses of nano-sized Co-based powders by carbothermal reduction for anode materials of lithium ion batteries

Seong-Hyeon Hong[a], Myoung Youp Song[b,*]

[a] Small and Medium Sized Corporate Supporting Department, Korea Institute of Materials and Science (KIMS), Affiliated with Korea Institute of Machinery and Materials, 797 Changwon-daero, Seongsan-gu, Changwon, Gyeonsangnam-do 51508, Republic of Korea

[b] Division of Advanced Materials Engineering, Research Center of Advanced Materials Development, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu, Jeonju 54896, Republic of Korea

ARTICLE INFO

Keywords:
Anode materials
Lithium ion battery
Spray drying
Discharge capacity
Nano-cobalt powder

ABSTRACT

Co oxide powders were synthesized by spray drying, calcining, and then ball milling. Nano-sized Co-based powders were then prepared by carbothermal reduction at 873 K, 1073 K, and 1173 K of the synthesized Co oxide powders. Then, the electrochemical properties of the electrodes made with the Co-based powders were examined to evaluate their suitability as anode materials for Li-ion batteries. It was reported that among Co, CoO, and Co_3O_4, Co_3O_4 had the best cycling performance. However, in this work, Co showed the best cycling performance. This means that the mechanisms of the cycling performance of CoO and Co which were synthesized by different heat treatment methods are different from each other. The initial discharge capacities of three electrodes made with the powders reduction-treated at 873 K, 1073 K, and 1173 K were similar and about 1100 mA h/g, respectively. However, the electrodes made with the powders reduction-treated at 873 K and 1073 K had the discharge capacities at the second cycle which were less than 50% of the discharge capacity of the electrode made with the powder reduction-treated at 1173 K. The electrode made with the powder reduction-treated at 1173 K had a discharge capacity of 750 mA h/g at the 20th cycle, demonstrating that this electrode had good cycling performance.

1. Introduction

Several different types of lithium-based rechargeable batteries [1,2] have drawn attention due to expectation of high energy densities. The carbon-based materials, used traditionally as anodes [3–5], have a theoretical capacity of 372 mA h/g, which is not sufficient. New anode materials with high capacities are thus necessary to be developed.

Ahn reported that reducing the particle size of the host material can buffer the volume expansion involved during charge and discharge [6]. Much work using nano-sized materials as electrodes has been carried out since nano-sized powders exhibit good electrochemical performances. The nano-sized powder can be synthesized by various methods like sol-gel [7], solvothermal [8], spray conversion [9], and pulsed wire evaporation (PWE) [10,11], pyrolysis [12], and hydrothermal methods [13,14].

Poizot et al. [15] synthesized nano-sized transition-metal oxides (MO, where M is Co, Ni, Cu, or Fe) to use anode materials for lithium ion batteries. They reported that the reversible electrochemical reaction mechanism of Li with transition-metal oxides such as CoO mostly involves a displacive redox reaction, implying reversible formation (CoO + 2Li → Li_2O + Co) and decomposition (Li_2O + Co → CoO + 2Li) of Li_2O.

Hong et al. [9] prepared a nano-sized Co_3O_4 powder using a spray conversion method consisting of spray drying of a metallic liquid solution, a calcination treatment, and a ball milling process. The lithium/cobalt oxide cell showed the first discharge capacity of 1100 mA h/g at a constant current density of 0.2 mA/cm^2 [9]. The discharge capacity of the Li/ Co_3O_4 cell drastically decreased with increasing cycle number. By increasing the carbon content of the anode, cycle life was improved. For a Co_3O_4 electrode containing 40 wt% carbon, the discharge capacity was over 400 mA h/g after 50 cycles [9].

Nano-sized cobalt powders were prepared by Kim et al. [11] using a pulsed wire evaporation method. The cobalt powder had a spherical shape with a diameter of less than 200 nm. A cobalt electrode was prepared from the nano-sized cobalt powder, acetylene black and polyvinylidene fluoride. During the first discharge, the Li/Co cell showed a plateau potential of 0.7 V and a capacity of 440 mA h/g. The nano-sized Co electrode had a stable reversible lithium storage capacity of approximately 280 mA h/g after 30 cycles.

Ahn [6] reported that nano-sized anode materials had high

---

[*] Corresponding author.
E-mail address: songmy@jbnu.ac.kr (M.Y. Song).

https://doi.org/10.1016/j.ceramint.2017.12.002
Received 18 October 2017; Received in revised form 1 December 2017; Accepted 1 December 2017

Please cite this article as: Hong, S.-H., Ceramics International (2017), https://doi.org/10.1016/j.ceramint.2017.12.002

discharge capacities but showed poor cycling performances. Carbon coating is thought to improve the cycling performances of anode materials by preventing the formation of solid electrolyte interphase (SEI) layers between anode material and electrolyte. Hong et al. [9] insisted that this carbon can improve the electrical contact between the active material and the current collector, which induces the most active utilization of the active material. Another possibility is that the carbon helps the expansion of cobalt-oxide particles be relaxed during lithium insertion and extraction [9].

Yue et al. [12] embedded Co nanoparticles in a carbon matrix via pyrolysis of polymeric cobalt phthalocyanine (PcCo) at 973 K in an argon atmosphere. The electrode prepared with this C/Co composite had a reversible capacity of over 600 mA h/g at a current of 50 mA/g after 40 cycles, and showed a better rate capability and a less hysteresis compared with the carbon not containing Co.

Chi et al. [13] reported a hydrothermal strategy to synthesize a Co_3O_4/graphene composite as anode material for high-performance lithium-ion batteries. The polyhedral Co_3O_4 particles were homogeneously anchored on graphene sheets. The obtained Co_3O_4/graphene composite displayed a large reversible capacity (~840 mA h/g after 50 cycles), an excellent cyclic stability, and a good rate capability in comparison with pure Co_3O_4 nanoparticles.

Kang et al. [14] prepared a Super P (conductive black)-enhanced CoO anode for lithium-ion battery by a hydrothermal process followed by a heating treatment. These composites exhibited superior electrochemical performances with a high Li-ion storage capacity of 1020 mA h/g at 100 mA/g and a good rate capability (with a Li-ion storage capacity of 770 mA h/g at 1000 mA/g) during charge-discharge process.

CoO/Co_3O_4/graphene nanocomposites were synthesized by Zhang et al. [16] through an easy, accessible method followed by annealing treatment, using graphene as the appropriate carrier to load CoO/Co_3O_4 nanoparticles because of its high surface area. The CoO/Co_3O_4/graphene nanocomposites as anode materials for lithium-ion batteries delivered initial discharge-charge capacities of 1093.4 and 825.3 mA h/g. The nanocomposite electrode showed an excellent rate capability and an impressive cyclability, as well as a high reversible capacity of 695.4 mA h/g after 70 cycles at a discharge-charge current density of 0.5 C (1 C = 890 mA/g).

Yin et al. [17] synthesized porous Co_3O_4 microspheres by an ultrasonic spray pyrolysis method without any template and organic additive assistance. When performed as a anode material for lithium-ion batteries, the as-prepared Co_3O_4 material had a good cycle property and a superior rate performance with a highly reversible capacity of 654 mA h/g at a current density of 400 mA/g [17].

Pan et al. [18] reported a strategy for fabrication of porous Co/Co_3O_4-C core-branch nanowire arrays. Using chemical bath deposition, electro-deposition, and annealing process, Co/Co_3O_4-C nanoflake branch was successfully assembled on the Co core nanowires forming the aligned core-branch nanowires with diameters of about 550 nm. A specific capacity of 608 mA h/g was obtained at 0.5 C after 200 cycles, much higher than unmodified Co_3O_4 nanoflake arrays (501 mA h/g at 0.5 C after 200 cycles).

In the present work, Co oxide powders were prepared by spray drying, calcining, and then ball milling. These Co oxide powders were thereafter ball milled with carbon powder and reduced at 873 K, 1073 K, and 1173 K, respectively, under argon atmosphere. Their electrochemical properties were then examined to evaluate their suitability as anode materials for Li-ion batteries.

2. Materials and methods

To prepare Co-dissolved solution, Co-nitrate [$Co(NO_3)_2.6H_2O$] (Jusei, Japan, 98%) and distilled water were dissolved at 1:1 wt ratio and stirred for 24 h. The Co-dissolved solution was then introduced at a 20 cc/min rate into a spray drying chamber in which the disc was rotating at 15,000 rpm. The temperatures of input air and output air were 523 K and 383–403 K, respectively. Agglomerated powders were removed by sifting the acquired powder through a sieve of 325 mesh (45 μm). Sieved powder was then heated to 773 K at a heating rate of 5 K/min, calcined at 773 K for 2 h, and cooled in the furnace to remove the components except metals. Since spray-dried nanoparticles were agglomerated, agglomeration was minimized through ball milling: 80 wt% spray-dried Co-oxide nanoparticles with 20 wt% carbon black were mixed in a stainless container (inner dia. 70 mm x inner length 80 mm, inner vol. 307 cc) with additional 55 cc of hexane and one kg of cemented carbide balls (dia. 6 mm) for 12 h. The ratio of spray-dried Co-oxide nanoparticles (80 wt%) to carbon black (20 wt%) was calculated with excess carbon after reduction from the reaction equation $Co_3O_4 + 4\,C \rightarrow 3Co + 4CO$ shown in Fig. 2. After ball milling, powders were reduction-treated at 873 K, 1073 K, and 1, 173 K, respectively, in an Ar atmosphere for 2 h.

The powders after spray drying, calcining, ball milling, and reduction treatment were analyzed by X-ray diffraction (Rigaku), BET (Brunauer-Emmett-Teller) surface-area measurements (ASAP 2000), and microstructure observation using FE-SEM (field-emission scanning electron microscope) (JEOL).

Electrochemical properties of the prepared nanoparticles as anodes of Li-ion batteries were measured as follows. The synthesized powder (85 wt%) was mixed with 10 wt% conducting carbon black and 5 wt% polyvinylidene fluoride (PVDF) binder and then dissolved in N-methyl-2-pyrrolidone (NMP) to prepare a slurry. The slurry was coated on Cu foil at 373 K and dried in a vacuum for 12 h. It was then subjected to rolling under a pressure of 100 kg/cm^2 [19]. The coated slurry was punched with a Φ14.6 mm punch. Cells for measurements were coin cells (type 2016). Li metal was used as counter and reference electrodes. Electrolyte was 1 M $LiPF_6$ dissolved in a 1: 1 (volume ratio) mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) [19]. Charge-discharge tests and cyclic voltammetry (CV) tests were performed using a charge-discharge tester (WBCS3000, WonATech Ltd.) [19]. Cells were charged and discharged at a current density of 0.2 mA/cm^2 in a voltage range of 0.001–2.5 V versus Li/Li$^+$. Cyclic voltammogram experiment was performed at a scanning rate of 1 mV/sec.

3. Results and discussion

The X-ray diffraction patterns of a spray dried precursor and the Co oxide powder synthesized by spray drying, calcining (for 2 h at 773 K), and then ball milling are shown in Fig. 1. The spray dried precursor

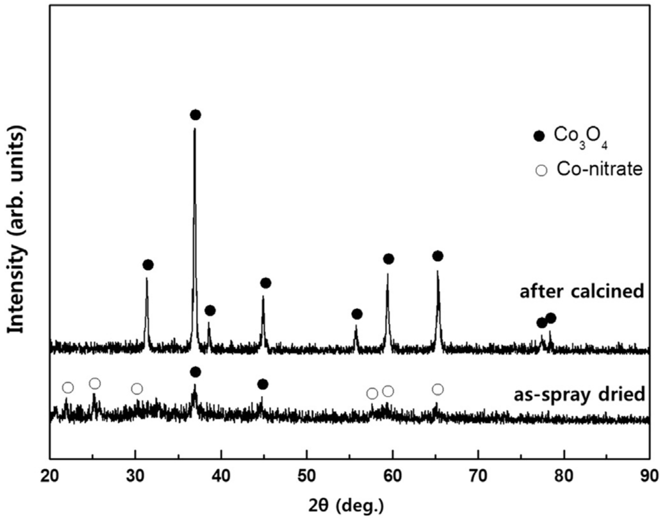

Fig. 1. X-ray diffraction patterns of a spray dried precursor and the Co oxide powder synthesized by spray drying, calcining (for 2 h at 773 K), and then ball milling.