



# Electrochemical properties of cobalt sulfide-carbon composite powders prepared by simple sulfidation process of spray-dried precursor powders



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## ABSTRACT

Cobalt sulfide-carbon composite powders were prepared by sulfidation of precursor powders obtained by spray drying. The precursor powders were composed of large particles with dimensions of several tens of micrometers and a hollow morphology with a thin-walled structure. The XRD pattern of the powders sulfidated at 200 °C showed Co<sub>9</sub>S<sub>8</sub> as the main phase and CoS as the minor phase. However, the XRD patterns of the powders sulfidated at 300 and 400 °C showed CoS as the main phase and Co<sub>9</sub>S<sub>8</sub>, Co<sub>3</sub>S<sub>4</sub>, and CoS<sub>2</sub> as the minor phases. The primary particle sizes of the powders sulfidated at 200, 300, and 400 °C were 80, 190, and 230 nm, respectively. Ultrafine cobalt sulfide crystals, a few nanometers in size, were uniformly distributed across the cobalt sulfide-carbon composite sheet. Dot-mapping images revealed that the carbon component was uniformly distributed throughout the composite powder. The optimum sulfidation temperature to obtain the composite powders with superior electrochemical properties was 300 °C. The initial discharge and charge capacities of the composite powders sulfidated at 300 °C at a current density of 1000 mA g<sup>-1</sup> were 1089 and 878 mA h g<sup>-1</sup>, respectively. The discharge capacity of the composite powders sulfidated at 300 °C became stable at around 790 mA h g<sup>-1</sup> for up to 70 cycles.

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## 1. Introduction

Carbon composites containing transition metal oxides, such as Co<sub>3</sub>O<sub>4</sub>, NiO, Mn<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, have been widely studied as anode materials for lithium-ion batteries (LIBs) because of the high electrical conductivity of carbon and the role of carbon as a buffering matrix [1–12]. In recent years, transition metal sulfides (M<sub>x</sub>S<sub>y</sub>, M = Zn, Cu, Ni, Fe, etc.) have attracted considerable attention as electrode materials for lithium-ion batteries (LIBs) because of their high storage capacity, low cost, and facile synthesis [13–29]. Metal sulfide-carbon composite powders have also been studied as electrode materials [30–44]. The inclusion of carbon improves the structural stability of the metal sulfides during cycling and also augments the conductance of the active materials.

The electrochemical properties of carbon composite materials strongly depend on their morphological characteristics. Therefore,

carbon composites containing transition metal oxides with various morphologies were developed as anode materials for LIBs. However, only metal sulfide-carbon composite materials with restricted morphologies have been studied in LIBs because of difficulties in synthesis. Li et al. prepared SnS-carbon composites with a net-like structure, in which SnS nanoparticles were dispersed homogeneously into carbon aerogel, via a precipitation reaction for use in lithium ion batteries [33]. High specific capacity and high rate performance were achieved by Wu et al. using iron sulfide-embedded carbon microspheres prepared via a solvothermal process [34]. High reversible capacity, excellent cycling stability, and high-rate capability were achieved by a nanocomposite prepared via a hydrothermal route and comprised of single-layer MoS<sub>2</sub>, graphene, and amorphous carbon [35]. The electrochemical properties of the bare cobalt sulfide and cobalt sulfide-carbon composite powders prepared by liquid solution and solid state methods were mainly investigated in the previous literatures [22–25,37–40]. However, in the liquid solution methods, the cobalt sulfide materials were prepared by complicated multi-step process.

Spray drying is a widely used industrial process for producing a dry powder from a liquid or slurry by rapidly drying with a hot gas. This method has already been employed to prepare nanoporous

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spherical materials for applications in lithium ion batteries [45–48]. In this study, cobalt sulfide-carbon composite powders composed of spherical and hollow particles were prepared by a two-step process. The cobalt oxide-carbon composite powders composed of spherical and hollow particles, obtained by the spray drying process, were sulfidated inside a tubular reactor using hydrogen sulfide gas formed by the decomposition of thiourea. The effects of the sulfidation temperature on the morphologies, crystal structures, and electrochemical properties of the cobalt sulfide-carbon composite powders were investigated.

## 2. Experimental

### 2.1. Material synthesis

A schematic diagram of the spray drying process is shown in Fig. S1. A liquid containing a high concentration of the product material was pumped to an atomizing device where it was transformed into a spray of small droplets. These droplets met a stream of hot air for drying. The resulting dry powder was separated from the humid air by centrifugal forces in a cyclone system. The temperatures at the inlet and outlet of the spray dryer were 350 °C and 150 °C, respectively. A two-fluid nozzle was used as the atomizer, and the atomization pressure was 0.3 bar. The spray solution was prepared by dissolving cobalt nitrate hexahydrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  and citric acid, as a chelating agent, in distilled water. The concentrations of cobalt nitrate hexahydrate and citric acid in the spray solution were 0.5 M and 0.3 M, respectively. The precursor powders obtained by the spray drying process were post-treated in air or  $\text{N}_2$  gas atmospheres at a temperature of 400 °C for 3 h to form cobalt oxide or cobalt oxide-carbon composite powders, respectively.

The simple sulfidation of the cobalt oxide and cobalt oxide-carbon composite powders, using hydrogen sulfide gas at temperatures between 200 and 400 °C for 6 h, produced the cobalt sulfide and cobalt sulfide-carbon composite powders, respectively. A small alumina boat containing the cobalt oxide-carbon composite powders was loaded into a larger alumina boat with a cover. The thiourea was loaded in the outside of the small alumina boat and inner side of the large alumina boat. The cobalt oxide-carbon composite powders were reacted with hydrogen sulfide gas. Reaction of melted thiourea and hydrogen gas supplied as the carrier gas produced the hydrogen sulfide gas.

### 2.2. Characterizations

The crystal structures of the cobalt sulfide and cobalt sulfide-carbon composite powders were investigated using X-ray diffraction (XRD, Rigaku DMAX-33) at the Korea Basic Science Institute (Daegu). The morphological characteristics of the powders were investigated using a scanning electron microscope (SEM, JEOL JSM-6060), field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), and a high-resolution transmission electron microscope (HR-TEM, FEI Tecnai™ 300 K).

### 2.3. Electrochemical measurements

The capacities and cycling performances of the powders were analyzed by constructing a 2032-type coin cell. The electrode was made by mixing 35 mg of the active powders with 10 mg of carbon black and 5 mg of sodium carboxymethyl cellulose (CMC) in distilled water. The size of the electrode was 1 cm × 1 cm and the mass loading was about 1.6 mg  $\text{cm}^{-2}$ . Lithium metal and a polypropylene film were used as the counter electrode and the separator, respectively. The electrolyte used was 1 M  $\text{LiPF}_6$ , dissolved in a mixture of fluoroethylene carbonate/dimethyl carbonates (FEC/DMC) with a volume ratio of 1:1 (TECHNO Semichem. Co.). The entire cell was

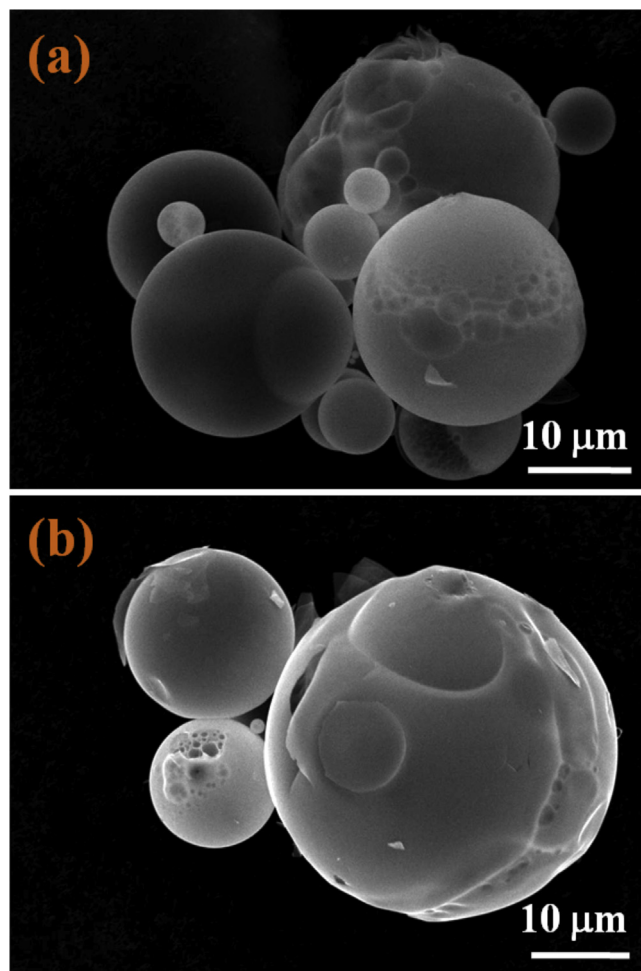


Fig. 1. Morphologies of the precursor powders prepared by spray drying process before (a) and after (b) post-treatment at 400 °C under nitrogen atmosphere.

assembled in a glove box under an argon atmosphere. The charge-discharge characteristics of the samples were measured by cycling through a potential range of 0.01–3.0 V at various current densities. Cyclic voltammetry measurements were carried out at a scan rate of 0.1  $\text{mV s}^{-1}$  in the range 0.01–3.0 V. Electrochemical impedance spectroscopy measurements of the electrodes were acquired in the frequency range between 500 k and 10 mHz at room temperature.

## 3. Results and discussion

The morphologies of the precursor powders, which were prepared by the spray drying process, before and after post-treatment at 400 °C under a nitrogen atmosphere, are shown in Fig. 1. The cobalt citrate, formed by chelation of the Co component with citric acid, exhibited good drying properties, even when the residence time of the droplets within the spray dryer was short, and high stability in the presence of water vapor. Consequently, the cobalt citrate powders could be easily collected by the cyclone system. The dried precursor powders formed from the cobalt citrate had poor gas penetration property during spray drying. Therefore, the resulting precursor powders were composed of large particles with dimensions of several tens of micrometers and a hollow morphology with a thin-walled structure, as shown in Fig. 1a. The post-treatment of the cobalt citrate powders under a nitrogen atmosphere at 400 °C produced cobalt oxide-carbon composite powders. The hollow morphology and thin-walled structure of the

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