



# Electrochemical properties of bare nickel sulfide and nickel sulfide–carbon composites prepared by one-pot spray pyrolysis as anode materials for lithium secondary batteries



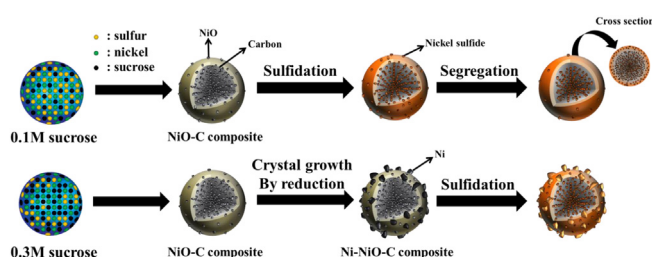
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## HIGHLIGHTS

- Spherical bare nickel sulfide and nickel sulfide–carbon composite powders are prepared by a one-step spray pyrolysis.
- Nickel sulfide nanocrystals with a size of a few nanometers are uniformly distributed inside the spherical carbon matrix.
- Nickel sulfide–carbon composite powders have an excellent discharge capacity of  $472 \text{ mA h g}^{-1}$  even after 500 cycles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Spherical bare nickel sulfide and nickel sulfide–carbon composite powders are prepared by a one-step spray pyrolysis. Submicron bare nickel sulfide particles with a dense structure have mixed crystal phases of  $\text{NiS}$ ,  $\text{Ni}_7\text{S}_6$ , and  $\text{Ni}_x\text{S}_6$ . The nickel sulfide–carbon composite powders prepared from a spray solution containing 0.1 M sucrose have a main crystal structure of  $\text{Ni}_7\text{S}_6$  phase with small impurity peaks of  $\text{Ni}_x\text{S}_6$  phase. A nickel oxide–carbon composite powder is first formed as an intermediate product in the front part of the reactor at  $800^\circ\text{C}$ . Fast decomposition of thiourea at this high temperature results in the evolution of hydrogen sulfide gas, which then forms the nickel sulfide–carbon composite powders by direct sulfidation of nickel oxide under the reducing atmosphere. Nickel sulfide nanocrystals with a size of a few nanometers are uniformly distributed inside the spherical carbon matrix. The nickel sulfide–carbon composite powders prepared with 0.1 M sucrose have an excellent discharge capacity of  $472 \text{ mA h g}^{-1}$  at a high current density of  $1000 \text{ mA g}^{-1}$ , even after 500 cycles, with the corresponding capacity retention measured after the first cycle being 86%.

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## 1. Introduction

Metal sulfides have been attracting a great deal of attention from researchers owing to their distinct electrical and optical properties compared to those of the corresponding metal oxides

[1]. A number of different compositions of metal sulfides have been considered for applications such as in batteries, catalysts, electrochromic devices, solar energy devices and so on [2–7]. In particular, nickel sulfides have been studied as potential active materials for lithium secondary batteries because of their high theoretical capacity characteristics [7–9]. However, one of the drawbacks of using nickel sulfides for such an application is that they exhibit poor electrochemical properties at high current densities. Various methods, such as applying dopants, coating layers, and forming

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composites, have been evaluated for improving the rate performances of nickel sulfide anode materials. Iron-doped nickel disulfide has demonstrated good cycling characteristics, with the iron atoms stabilizing the crystal structure by replacing some of the nickel atoms and slowing down the reduction in capacity [10]. Takeuchi et al. achieved improvements in the electrochemical properties of nickel sulfide by applying a surface coating of titanium dioxide or zirconium dioxide [11], while Mahmood et al. prepared a composite with nitrogen-doped graphene [12]. Graphene is well known as a support material for use in applications such as this, owing to its superior electrical conductivity, flexible volume expansion, high surface-to-volume ratio, and chemical stability [8,13,14]. However, the preparation of spherical nickel sulfide–carbon composite powders with high density and their electrochemical properties have not been studied in detail.

Nickel sulfide-based materials prepared using solid-state reactions and solution methods have been commonly used to prepare the anode of lithium secondary batteries [12,15]. As an alternative approach, the gas-phase spray pyrolysis technique has a number of advantages for the preparation of spherical metal sulfide particles. Sulfide powders containing a single metal have been formed from a droplet containing a metal salt and sulfur source in a one-pot process. Various types of metal sulfides, including zinc, copper, cadmium, and molybdenum compounds, have been successfully produced using the spray pyrolysis process [16–20]. However, to the best of our knowledge, the electrochemical properties of metal sulfide powders prepared using this particular technique have not been reported thus far.

In this study, bare nickel sulfide and nickel sulfide–carbon composite powders were first prepared using a simple one-pot spray pyrolysis process. The carbon contents of the composite powders were controlled by changing the concentration of the sucrose carbon source dissolved in the spray solutions. The electrochemical properties of the resulting nickel sulfide–carbon composite powders were subsequently evaluated and compared to those of the bare nickel sulfide powders.

## 2. Experimental

Bare nickel sulfide and nickel sulfide–carbon composite powders were prepared by ultrasonic spray pyrolysis. A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets. The inner diameter and length of the quartz reactor in the generator were 55 mm and 1.2 m, respectively. The reactor temperature was maintained at 800 °C, and the flow rate of the nitrogen used as the carrier gas was fixed at 5 L min<sup>-1</sup>. The spray solution was prepared by dissolving nickel nitrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Junsei, Japan] and thiourea [HN<sub>2</sub>NCSNH<sub>2</sub>, Junsei] in distilled water. A thiourea quantity in excess of 100% of the stoichiometric amount necessary to form nickel sulfide was added to the spray solution. Sucrose was used as the carbon source for forming the nickel sulfide–carbon composites. The overall concentrations of nickel and sulfur components in the spray solution were 0.5 M, and the concentration of sucrose dissolved in the spray solution was varied from 0.03 to 0.3 M.

The crystal structures of the bare nickel sulfide and nickel sulfide–carbon composites were investigated using X-ray diffraction (XRD, Rigaku DMAX-33) using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at the Korea Basic Science Institute (Daegu). The morphologies of the precursor powders were characterized using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (TEM, JEOL JEM-2010). The carbon contents of the nickel sulfide–carbon composite powders were measured from the energy dispersive spectroscopy (EDS) spectra. The Brunauer–Emmett–Teller (BET) surface

areas of the powders were measured using nitrogen gas as the adsorbate. The thermal behaviors of the bare nickel sulfide and nickel sulfide–carbon composite were studied by thermal gravimetric analysis (TGA, SDTA851) and differential scanning calorimeter (DSC, DSC823). The samples were heated at the heating rate of 10 °C min<sup>-1</sup> in the temperature range of 30–900 °C.

The capacities and cycle properties of the bare nickel sulfide and nickel sulfide–carbon composites were measured using 2032-type coin cells. The electrodes were prepared using a slurry consisting of 70 wt% active anode material, 20 wt% carbon black (Super-P) as a conductive material, and 10 wt% binder composed of sodium carboxymethyl cellulose (CMC) on copper foil. Lithium metal and a microporous polypropylene film were used as the counter electrode and separator, respectively. Lithium hexafluorophosphate (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio with 2 wt% vinylene carbonate (VC) was used as the electrolyte. The entire cell was assembled under an argon atmosphere in a glove box. The charge/discharge characteristics of the samples were measured at various current densities in the voltage range 0.01–3.0 V. Cyclic voltammetry measurements were carried out at a scan rate of 0.1 mV s<sup>-1</sup> between 0.01 and 3 V. Electrochemical impedance spectra of the bare nickel sulfide and nickel sulfide–carbon composite were analyzed in the frequency range between 100 kHz and 10 MHz at room temperature with a signal amplitude of 5 mV.

## 3. Results and discussion

The crystal structures of the bare nickel sulfide and nickel sulfide–carbon composite powders prepared by spray pyrolysis are shown in Fig. 1. The nickel sulfide powders prepared without sucrose had mixed crystal structures consisting of NiS, Ni<sub>7</sub>S<sub>6</sub>, and Ni<sub>x</sub>S<sub>6</sub> phases. The peak intensities of the NiS phase can be seen to decrease with increasing concentration of sucrose dissolved in the spray solution. The nickel sulfide–carbon composite powders prepared from the spray solution with 0.3 M sucrose had a pure crystal structure of Ni<sub>7</sub>S<sub>6</sub> phase. A small peak corresponding to Ni<sub>x</sub>S<sub>6</sub> [JCPDS card no. 00-051-0718] can be observed in the XRD pattern of the composite powders prepared with 0.1 M sucrose. No peaks resulting from nickel oxide are evident in the XRD patterns of the powders, irrespective of the concentration of sucrose used, demonstrating that the bare nickel sulfide and nickel sulfide–carbon composite powders were successfully prepared even with only an 8 s residence time inside the hot-wall reactor. The nickel sulfide–carbon composite powders prepared from the spray

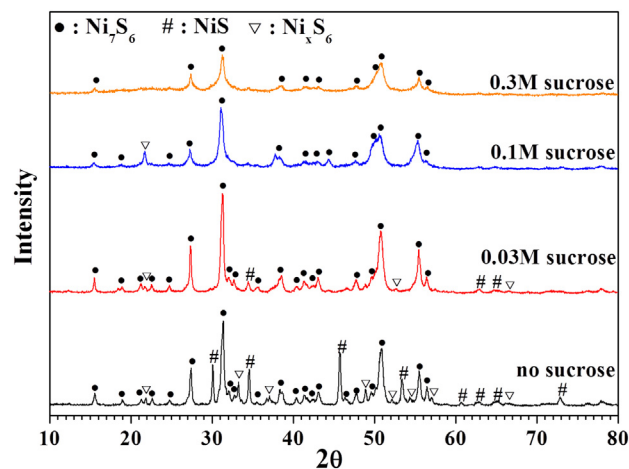


Fig. 1. XRD patterns of the bare nickel sulfide and nickel sulfide–carbon composite powders prepared by spray pyrolysis.

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