



Scalable synthesis of NiMoO₄ microspheres with numerous empty nanovoids as an advanced anode material for Li-ion batteries



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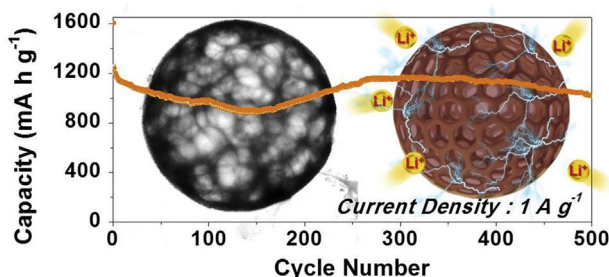
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HIGHLIGHTS

- NiMoO₄ microspheres with empty nanovoids are produced by spray-drying process.
- Uniquity of structure enables longer cycle life and higher quality performances.
- NiMoO₄ microspheres exhibit excellent characteristics for Li-ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Closely in line with advances in next-generation energy storage materials, anode materials for lithium-ion batteries (LIBs) with high capacity and long cycle life have been widely explored. As part of the current effort, nickel molybdate (NiMoO₄) microspheres with empty nanovoids are synthesized via spray drying process and subsequent one-step calcination in air. Dextrin in the atomized droplet is phase segregated during the spray drying process and calcined in air atmosphere, resulting in numerous empty nanovoids well-distributed within a microsphere. The empty nanovoids alleviate volume expansion during cycling, shorten lithium-ion diffusion length, and facilitate contact between electrode and electrolyte materials. Along with the high discharge capacity of NiMoO₄ material, as high as 1240 mA h g⁻¹ for the 2nd cycle at a high current density of 1 A g⁻¹, uniqueness of the structure enables longer cycle life and higher quality performances. The discharge capacity corresponding to the 500th cycle is 1020 mA h g⁻¹ and the capacity retention calculated from the 2nd cycle is 82%. In addition, a discharge capacity of 413 mA g⁻¹ is obtained at an extremely high current density of 10 A g⁻¹.

1. Introduction

With the continuously surging demand for eco-friendly and sustainable energy supplies, lithium ion batteries (LIBs) have received tremendous attention worldwide and are currently the dominant power source for portable electronic devices [1–22]. However, for lithium ion batteries to be used in large-scale energy applications, such as low-

emission electric vehicles, further improvements in terms of capacity and rate capability are needed [1–9]. The design of advanced anode materials with optimum composition for lithium ion batteries is considered critical to achieving high electrochemical performance [10–18]. Transition metal molybdates are promising candidates for electrode materials for LIBs in view of their high capacity due to a variety of reversible reduction/oxidation activities resulting from multiple

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valence states [12–18]. Particularly, NiMoO₄ has received considerable attention owing to the high electrochemical performance of nickel ion and comparatively high electrical conductivity of molybdenum [16–18]. Unfortunately, selecting the right material alone is insufficient for designing optimum electrode materials due to repetitive volume changes during the lithiation/delithiation process, resulting in rapid capacity fading [16–21]. Material architecture of a highly effective surface that accommodates volume expansion is a powerful tool for enhancing battery performance [16–21].

The introduction of empty nanovoids within a microsphere has greatly improved electrochemical performance, despite the fact that the volumetric capacity is impaired due to the empty space [22–27]. Recently, Wang et al. synthesized mesoporous Fe₂O₃ spherical particles by spray pyrolysis with mesopores providing additional voids that alleviate structural stress during electrochemical reaction [26]. They allowed shorter lithium ion diffusion pathway, ensuring high rate performance. Cho et al. synthesized multiroom-structured Co₃O₄ microspheres by a spray pyrolysis process using hydrophilic dextrin, without applying template nanobeads, and proved the effectiveness of empty nanovoids in LIBs [27]. Inspired by these researches, spray drying method was adopted to synthesize microspheres with empty nanovoids for application in anode materials for LIBs. To the best of our knowledge, multiroom-structured microspheres applied as anode material for LIBs have not been synthesized by spray drying process. Spray drying is commonly used for large-scale production of spherical microspheres [28–32].

We herein report a facile synthesis method for transition metal molybdate oxide microspheres with empty nanovoids. Notably, nanovoids within the microspheres could be introduced without the use of surfactant or removable hard templates. A pilot-scale spray drying process and subsequent heat treatment in air formed empty nanovoids by decomposition and combustion of phase-segregated dextrin. The lithium ion storage performance of the multiroom-structured NiMoO₄ microsphere with empty nanovoids is compared with its counterpart, a NiMoO₄ microsphere prepared from a spray solution without dextrin via an identical process. Along with the high capacity of multi-component transition metal oxide material, long cycle life up to 500 cycles was achieved for the NiMoO₄ microspheres, owing to the structural merits of tens of empty nanovoids distributed within the microspheres.

2. Experimental

2.1. Sample preparation

The NiMoO₄ microspheres with empty nanovoids were synthesized via a spray drying process and subsequent calcination step in air. The pilot-scale spray drying system shown in Fig. S1 was used to prepare the dense spherical microspheres. The spray drying solution was prepared by dissolving 0.075 M (NH₄)₆Mo₇O₂₄·4H₂O (98%, Daejung), 0.075 M Ni(NO₃)₂·H₂O (98%, Sigma Aldrich), and 40 g L⁻¹ of dextrin [(C₆H₁₀O₅)_n, Samchun] in distilled water. After vigorous stirring, the homogeneous solution was pumped to a two-fluid nozzle and then atomized at a pressure of 2.0 bar. Spray dryer inlet and outlet temperatures were adjusted to 300 °C and 120 °C, respectively. The spray-dried microspheres were consecutively loaded onto an alumina boat and placed in a quartz tube reactor and heated to 300, 400, and 500 °C at a rate of 10 °C min⁻¹ under air atmosphere.

2.2. Characterization techniques

The morphologies of the prepared microspheres were observed using field emission scanning electron microscopy (FE-SEM; Hitachi, S-4800) and field emission transmission electron microscopy (FE-TEM; JEOL, JEM-2100F). Crystallographic analysis was performed at the Korea Basic Science Institute (Daegu) via X-ray diffraction (XRD; X'Pert PRO MPD) using Cu-Kα radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron

spectroscopy (XPS; Thermo Scientific K-Alpha) with focused monochromatic Al-Kα radiation at 12 kV and 20 mA was used to determine the compositions of the specimens. The surface areas of the microspheres were determined using the Brunauer–Emmett–Teller (BET) method with N₂ as the adsorbate gas. Thermogravimetric analysis (TGA) was performed with a Pyris 1 TGA (Perkin Elmer, temperature range = 25–800 °C, heating rate = 10 °C min⁻¹, static air atmosphere) instrument.

2.3. Electrochemical measurements

The electrochemical properties of the prepared microspheres were analyzed by constructing 2032-type coin cells. The anode was prepared by mixing the active material, carbon black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1. Li metal was used as the counter-electrode and microporous polypropylene film was used as the separator. The electrolyte was produced by dissolving 1 M LiPF₆ in a mixture of fluoroethylene carbonate/dimethyl carbonate (FEC/DMC; 1:1 v/v). The discharge/charge characteristics of the samples were investigated by cycling over a potential range of 0.001–3 V at various current densities. Cyclic voltammograms were acquired at a scan rate of 0.1 mV s⁻¹. The dimensions of the negative electrode containing the microspheres were 1 cm × 1 cm with a mass loading of approximately 1.2 mg cm⁻². The electrochemical impedance was measured over a frequency range of 0.01 Hz–100 kHz via electrochemical impedance spectroscopy (EIS).

3. Results and discussion

The formation mechanism of empty nanovoids constituting the multiroom-structured NiMoO₄ microsphere prepared from the spray drying process and subsequent oxidation is illustrated in Scheme 1. Each atomized droplet was dried and formed microspheres comprising ammonium molybdate, nickel nitrate, and dextrin. SEM images of the spray-dried product with dense structure are shown in Fig. S2. Dextrin was phase-segregated during the spray drying process and subsequent oxidation caused dextrin decomposition, yielding the NiMoO₄/C or NiMoO₄ microspheres with empty nanovoids, depending on the post-treatment temperatures.

The morphologies of the NiMoO₄/C microspheres (denoted as NiMoO₄/C-A3) formed by oxidation of the spray-dried product at 300 °C are shown in Fig. 1. The SEM and TEM images in Fig. 1a and b revealed the microspheres with spherical shape and non-aggregation characteristics. Fractured microspheres in the magnified SEM image in Fig. 1a and TEM image in Fig. 1b–d clarify the nanorooms constituting the multiroom-structured microspheres. The TEM image presented in Fig. 1d shows the close-up framework of the microsphere. Ultrafine nanocrystals were embedded in the amorphous carbon matrix, which restricted the growth of NiMoO₄ crystallites, and thus were hardly distinguishable from the TEM image. The high resolution TEM image shown in Fig. 1e shows a lattice fringe separated by 2.05 Å which is, using the Bragg's law, calculated as 44.1° in the JCPDS card #12-0348. The selected area electron diffraction (SAED) pattern shown in Fig. 1f further elucidates the crystal structure of NiMoO₄. The d-spacing values of 2.48, 2.05, and 1.52 Å are calculated as 36.2, 44.1, and 60.7°, respectively, in the JCPDS card #12-0348. Unfortunately, the crystal planes corresponding to the d-spacing values are undefined to the best of our knowledge. Elemental dot mapping images shown in Fig. 1g revealed uniformly distributed Ni, Mo, and C throughout the multiroom-structured microsphere. Carbon remaining within the structure was confirmative, for the oxidation temperature was not high enough.

The morphologies of the multiroom-structured NiMoO₄ microspheres oxidized at 400 °C (denoted as NiMoO₄-A4) and 500 °C (denoted as NiMoO₄-A5) are shown in Figs. 2 and 3, respectively. NiMoO₄-A4 and NiMoO₄-A5 microspheres share similar morphologies with NiMoO₄/C-A3. However, individual nanocrystal was clearly seen from

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