Synthesis and lithium storage properties of MoS$_2$ nanoparticles prepared using supercritical ethanol

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HIGHLIGHTS

- A new supercritical ethanol route was developed to synthesis MoS$_2$ nanoparticles.
- Increasing calcination temperature led to decrease interlayer spacing.
- 500 °C-calcined MoS$_2$ delivered a large initial charge capacity of 1045 mAh g^{-1}.
- Higher temperature-calcined MoS$_2$ particles exhibit better cycling performance.

ARTICLE INFO

ABSTRACT

Nanostructured MoS$_2$ particles were synthesized in a very short reaction time of 10 min via a simple supercritical ethanol route for prospective application as an anode material for lithium ion batteries. The as-synthesized MoS$_2$ nanoparticles had a randomly oriented nanoplate structure with a Brunauer–Emmett–Teller (BET) surface area of 67.7 m^2 g^{-1} and a porosity of 59.6%. The as-synthesized samples were subjected to calcination at various temperatures in the range of 500–800 °C under H$_2$S/Ar and evaluated for use as anode materials in Li ion batteries. Increasing the calcination temperature from 500 to 800 °C led to a decrease of the interlayer distance from 0.68 to 0.61 nm and a decrease of the BET surface area from 44.8 to 7.53 m^2 g^{-1}. The samples calcined at low temperature delivered larger initial capacities (977–1342 mAh g^{-1}), while the samples calcined at high temperature exhibited better cycling performance and higher first coulombic efficiency (86–89%). MoS$_2$ calcined at 700 and 800 °C gave rise to reversible discharge capacities of 754 and 818 mAh g^{-1} at 100 mA g^{-1}, respectively, without the use of composite structures or carbonaceous supports.

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1. Introduction

In recent years, rechargeable lithium-ion batteries (LIBs) have received a great interest as power sources for plug-in hybrid electric vehicles (PHEVs), electric vehicles (EVs) and energy storage systems [1]. Although graphite is currently employed as the commercial anode material for LIBs, the low theoretical capacity (372 mAh g^{-1}) and the safety issues associated with the low Li ion insertion voltage make graphite unsuitable for use in large-scale energy storage applications [2]. In the quest to achieve high power densities, safety, and good cycling stability, various investigations have been conducted to develop new electrode materials [1–3]. Among the developed electrode materials, layered transition metal sulfides, such as MoS$_2$, WS$_2$, ZrS$_2$, and SnS$_2$, have piqued the interest of researchers as potential candidates for anode materials owing to their high theoretical capacities and unique layered structures [4–10]. MoS$_2$ has an inorganic graphene-analog layered structure that consists of molybdenum atoms sandwiched between two layers of closely packed sulfur atoms; the two-dimensional molecular layers are weakly linked by van der Waals interactions [11,12]. The theoretical capacity of MoS$_2$ is much

higher (669 mAh g^{-1} based on the conversion reaction: $MoS_2 + 4Li + 4e^- \leftrightarrow Mo + 2Li_2S$) than that of the commercial graphite-based anode. The exfoliated and loosely stacked S–Mo–S layered structure of MoS_2 may facilitate Li ion insertion and extraction without significant volume change compared to other conversion-based anode materials [6,13]. In addition, the higher lithium-ion insertion voltage relative to that of the commercial graphite anode makes MoS_2 a safe anode material [14]. The poor capacity retention and the low rate capability associated with MoS_2 have been overcome by designing nanostructured morphologies [14–24], by controlling the spacing of the MoS_2 layers [23,25,26], by incorporating carbon supports [27–34] or by forming composites with metal oxides phase [35].

Various methods have been employed to synthesize nanostructured MoS_2, including sacrificial template-based methods [16,17,19], vacuum-assisted impregnation [26], hydrothermal [14,15,22–24], solvothermal [18], rheological phase transition [20], and prelithiation [21] techniques. The preparation of various MoS_2 morphologies with diverse nanostructures such as nanowalls [14], 3D flowers [15], hierarchical hollow nanoparticles [18,19], nanospheres [24], nanoflowers [23], and mesoporous particles [16,26] has been widely attempted to enhance the electrochemical performance of lithium ion batteries. However, long reaction times, extensive use of toxic chemicals, generation of chemical wastes, complicated multi-step synthetic procedures, and the use of expensive structure-directing additives impede the practical application of these methods. Thus, fabrication of MoS_2 with high electrochemical performance via a facile method remains a challenge.

In recent years, supercritical fluids have been intensively studied as effective media for synthesis of nanomaterials due to their unique properties, including gas-like diffusivity, low viscosity, density closer to that of liquid, and extremely high supersaturation ratio [36–39]. For example, supercritical hydrothermal synthesis has been exploited in the synthesis of nano-sized active materials for use in LIBs. These materials include $LiCoO_2$ [40], $LiMn_2O_4$ [41], $LiFePO_4$ [42–45], $Li_4Ti_5O_{12}$ [46,47], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [48], and Li_2FeSiO_4 [49]. The use of supercritical alcohols conferred unique properties to the active materials; for example, the generation of hierarchical structures and surface modification by organic moieties generated from the alcohols in the supercritical state was observed [50–52]. These features were beneficial for improving the electrochemical performance of various types of active materials, including $Li_4Ti_5O_{12}$ [53,54], TiO_2 [55], and ZnO [56]. Supercritical alcohols have also been used in the synthesis of high-performance next-generation active materials such as $LiMPO_4$ (M = Fe, Mn, Co) nanocrystals [57–59], Li_2MSiO_4 (M = Fe, Mn, CO) nanosheets [60], and reduced graphene oxides [61–63]. Herein, we report the inceptive execution of the synthesis of MoS_2 nanoparticles using supercritical ethanol (scEtOH, T_c = 243 °C, P_c = 6.4 MPa). The size, surface area, porosity, morphology, and phase structure of the MoS_2 particles synthesized in scEtOH are discussed. The effect of the calcination temperature on the morphology and electrochemical properties are described in detail.

2. Experimental

2.1. Materials

Bis(acetylacetonato)dioxomolybdenum(VI) ([$CH_3COCH = C(O–)CH_3$]$_2MoO_2$, $MoO_2(acac)_2$, purity ⩾95%), sodium sulfide (Na$_2$S, purity ⩾97%) and anhydrous ethyl alcohol (C_2H_5OH, purity ⩾99.5%) were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received. Poly(vinylidene difluoride) (PVDF, Kureha Chem. Co., Tokyo, Japan) and 1-methyl-2-pyrrolidinone

(NMP, purity >98 wt%, Alfa-Aesar, MA, USA) were also used without further purification.

2.2. Synthesis of MoS_2

The synthesis of MoS_2 nanoparticles in scEtOH was conducted using a SUS 316 tube reactor with an inner volume of 11 mL, manufactured by the Hanyang Precision Company (Seoul, Korea). A predetermined amount of Na$_2$S was dissolved in 24 mL of ethanol with vigorous stirring at room temperature. When a clear solution was formed, the desired amount of $MoO_2(acac)_2$ was dissolved in the Na$_2$S/ethanol solution with vigorous stirring. A 4 mL aliquot of the solution mixture was loaded into the reactor. The reactor was then immersed in a molten salt bath with the temperature maintained at 400 °C. After the desired reaction time, the reactor was quenched in a cold water bath. The particles formed in the reactor were collected, carefully washed five times with ethanol to remove residual organic species, and dried in a vacuum oven at 70 °C for 12 h. The as-synthesized particles were then calcined at temperatures ranging from 500 to 800 °C for 5 h in 5% H_2S/Ar at a flow rate of 100 mL min^{-1}. The calcined samples were designated as MoS_2-500, MoS_2-600, MoS_2-700, and MoS_2-800 according to their calcination temperatures.

2.3. Characterization

Analysis of the crystalline phase of the samples was conducted using a D/Max-2500 V/PC Rigaku X-ray diffractometer (XRD, Tokyo, Japan) with Cu-K_α radiation at 40 kV and 50 mA. The diffraction patterns were acquired in the 2θ range of 10–80°. X-ray photoelectron spectroscopic (XPS) analysis of the samples was performed using a PHI 5000 Versa Probe (ULVAC-PHI Inc., Kanagawa, Japan) spectrometer. The morphologies of the samples were observed using a JEOL JSM-7500F field emission-scanning electron microscope (FE-SEM, JEOL USA, Inc). High resolution transmission electron microscope (HR-TEM) images were taken using an S/TEM FEI Titan Cubed G2 60-300 (FEI Co., Ltd., OR, USA) instrument equipped with a spherical aberration corrector at the imaging part, a monochromator, and a high brightness gun. All HR-TEM images were collected at an operating voltage of 80 kV in order to minimize damage to the samples induced by the high energy electron beam. Before acquiring the high resolution images, the spherical aberration corrector was tuned to set the third-order spherical aberration below 5 μm. All other aberrations, such as coma and three- and four-fold astigmatisms, were set to the minimum values. The monochromator was intermittently engaged to reduce the effect of chromatic aberration. Thus, all of the HR-TEM images were almost free of the imaging artifacts induced by various aberrations. Raman spectra were recorded using a LabRAM HR800 confocal Raman microscope (HORIBA Jobin Yvon). The Brunauer–Emmett–Teller (BET) surface area was measured using a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). The functional groups on the surface of the samples were characterized using a NICOLET iS10 Fourier-transform infrared (FT-IR) spectrometer (Thermo Electron Co., NJ, USA).

2.4. Measurement of electrochemical properties

The electrochemical measurements were conducted using the CR2032 type coin-cell configuration. The working electrode was composed of 70 wt% active material, 10 wt% acetylene black as a conducting agent, and 20 wt% PVDF as a binder. After blending with NMP, the slurry was uniformly cast onto a Cu foil to prepare the electrode film. The film was then dried on a heating board at 80 °C for 24 h to remove the solvent. The electrode film was punched into discs (diameter: 15 mm; area: 1.77 cm^2) and