



Low-crystallinity molybdenum sulfide nanosheets assembled on carbon nanotubes for long-life lithium storage: Unusual electrochemical behaviors and ascending capacities

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ABSTRACT

Low-crystallinity molybdenum sulfide (LCMS, Mo:S = 1:2.75) nanosheets synthesized by a facile and low temperature solvothermal method is now reported. The as-prepared LCMS anode material is composed of MoS₂ layers mixed with amorphous MoS₃, which leads to an unusual electrochemical process for lithium storage compared to typical MoS₂ anode. The existence of MoS₃ and Mo (VI) provide strong adsorption and binding sites for polar polysulphides, which compels abundant sulfur to turn into new-formed MoS₃ rather than diffuse into electrolyte. To fully utilize this novel electrochemical process, LCMS is decorated on carbon nanotubes, obtaining well-dispersed CNTs@LCMS. As electrode material for lithium storage, CNTs@LCMS exhibits a noticeable ascending trend in capacity from 820 mA h g⁻¹ to 1350 mA h g⁻¹ at 100 mA g⁻¹ during 130 cycles. The persistent ascending capacity is ascribed to the increasing lithium storage caused by new-formed MoS₃, combined with the reduced volume change benefiting from well-dispersed CNTs@LCMS. Furthermore, the ascending performance is proved to be able to effectively extend the circulation life (up to 200%) for lithium-ion batteries by mathematical modeling and calculation. Accordingly, the CNTs@LCMS composite is a promising anode material for long-life lithium-ion batteries.

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1. Introduction

Lithium-ion secondary batteries, with high specific energy and power densities, have dominated the power source field for portable electronic devices [1–5]. In order to meet the increasing huge power requirements of electric vehicles and the power storage for certain renewable energy sources, such as solar and wind energy, enormous efforts have been made to develop high-performance lithium-ion batteries (LIBs), especially the electrode materials [6–10]. In this context, many metal oxides or sulfides

have been intensively explored as alternative anode materials for lithium storage due to their relatively high energy density, environmental friendliness and low-cost [3,6,8]. In particular, MoS₂ has been considered as an attractive LIBs anode material in view of its facile synthesis and the capability to allow easy lithium ions insertion/extraction, enabling its assembly with diverse substrates and delivering a high theoretical specific capacity of 670 mA h g⁻¹ [11]. Various MoS₂ nanostructures such as nanoplates [12], nanotubes [13] and nanoflowers [14] have been reported for lithium storage as LIB anodes which showed high capacities. However, large volume changes often occur in the MoS₂ anode during repeated charge and discharge process, which causes pulverization and aggregation, hence resulting in quick capacity fading upon cycling. Furthermore, the reaction process of MoS₂ generally involves insulating polysulfides (Li₂S_x, 1 < x < 8) which could easily dissolve in liquid electrolyte, causing dissolution loss of electrode, deteriorated the conductivity of the electrolyte and the electrode, thus leading to capacity fading [15–17].

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Amorphization of active materials has been considered as an effective approach to improve the cycling stability and specific capacity. Firstly, the isotropic and open structure in amorphous materials can effectively tolerate the anisotropic expansion caused by the insertion of lithium ions and reducing stresses deriving from phase transition [18,19]. The comparatively slight volume changes were demonstrated in the amorphous silicon and tin oxide based anodes [20–22]. Secondly, amorphous materials possess a lower reactions change in Gibbs free energy (ΔG) compared to its crystallinity counterpart, which contributes to the enhanced reversibility of conversion reaction for amorphous anode [23]. For example, the amorphous Fe_2O_3 , MnO_x and MoO_2 have been reported to exhibit higher capacity and better cyclability than crystallinity one [23–25]. In addition, amorphous MoS_3 present steadily reversible electrochemical performance for lithium storage and Mo (VI) with high affinity for sulfur-containing molecules can reduce the dissolution of polysulfides, benefiting the capacity and cyclability of electrode [19,26]. On the other hand, active materials were usually immobilized into/onto various matrices to suppress their capacity fade during cycling, such as carbon nanofiber, carbon nanotube (CNT), graphene [26–28].

In this work, we report the synthesis of a low-crystallinity molybdenum sulfide (LCMS, Mo:S = 1:2.75) by a facile and low temperature solvothermal approach. The LCMS is likely the mixture of layered MoS_2 and amorphous MoS_3 , indicated by XPS, ICP and TEM characterization. The LCMS shows an unusual electrochemical behaviour in the lithium ion storage, distinct from those of previous studies of MoS_2 -based materials [26,29,30] and MoS_x/CNTs [31]. When the LCMS was directly loaded on pristine CNTs to build a new composite anode (CNTs@LCMS) for LIBs, a phenomenon of ascending capacity upon cycling appears. Furthermore, a mathematical modelling and calculation demonstrates that the phenomenon of ascending capacity caused by this abnormal electrochemical process can effectively extend the circulation life of lithium-ion batteries.

2. Experimental section

2.1. Materials synthesis

2.1.1. Chemicals

The carbon nanotubes (CNTs) were purchased from Nanocyl, Belgium. The $(\text{NH}_4)_2\text{MoS}_4$ powder and *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Australia. All chemicals were used as received without further purification.

2.1.2. Preparation of the CNTs@LCMS composite

0.1 g of CNTs was dispersed into 30 mL of *N,N*-dimethylformamide (DMF) by ultrasonication for 20 min. Then, 0.22 g of $(\text{NH}_4)_2\text{MoS}_4$ powder was added in the solution. After stirring for 10 min, the homogeneous solution was transferred into a 35 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 24 h. The autoclave was then left to cool down to room temperature naturally. The black precipitate was collected by centrifugation, thoroughly washed with deionized water and ethanol for several times and dried at 70 °C for 12 h in vacuum.

For comparison, the as-prepared CNTs@LCMS composite was further annealed at 800 °C in an atmosphere of 5% of H_2 balanced by Ar at a ramping rate of 5 °C min^{-1} and maintained at this temperature for 2 h in order to convert amorphous MoS_3 into high-crystallinity MoS_2 , resulting in the CNTs@ MoS_2 composite.

2.1.3. Preparation of LCMS clusters

LCMS clusters were prepared by the same method as mentioned above, in the absence of CNTs.

2.2. Characterization

The distribution, size and morphology of the as-prepared samples were characterized by the scanning electron microscopy (SEM) (FEI SIRION 200). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDX mapping studies were carried out on a probe-corrected transmission electron microscope operating at 200 kV (FEI Tecnai F20). The chemical compositions and structures of the as-prepared samples were analysed by X-ray diffraction (XRD) (Bruker D8 Advance X-ray diffractometer, Cu-K α radiation $\lambda = 0.15406$ nm) and X-ray photoelectron spectroscopy (XPS) (AXIS Ultra-DLD, Kratos Analytical, Manchester, UK, using monochromated Al K α radiation). The exact Mo:S molar ratio in the LCMS clusters was also measured by the inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 730). The LCMS clusters were digested into the solution using a mixed acid method. Then the resulting solution was diluted appropriately and measured for the Mo and S elements (molar ratio, Mo: S = 1:2.75) by the ICP-OES.

2.3. Electrochemical measurements

The working electrodes were fabricated by coating a slurry containing 80 wt% of active materials (CNTs@LCMS, CNTs@ MoS_2 or LCMS clusters), 10 wt% of acetylene black (Super-P), and 10 wt% of polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidinone onto a copper foil and dried at 100 °C in vacuum for 12 h before pressing. Standard CR2032-type coin cells were assembled in an Ar-filled glovebox (KIYON, Korea) by using the as-prepared anode, Li metal foil (0.4 mm thick) as the counter electrode, and a separator (Solupor 7P03A). The electrolyte was composed of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (V/V = 1:1). The cells were aged for 12 h before the measurements. Galvanostatic discharge–charge (GDC) experiments were performed at different current densities in the voltage range of 0.01–3.00 V with a multichannel battery tester (Maccor, Inc, USA). Cyclic voltammetry (CV) measurements were conducted by the electrochemical workstation (Solartron Potentiostat and Impedance Analyser, UK). Electrochemical impedance spectra (EIS) were measured using the same electrochemical workstation by applying an AC voltage of 10 mV amplitude over the frequency range from 100 kHz to 0.1 Hz.

3. Results and discussion

The bare low-crystallinity molybdenum sulfide (LCMS) powder and CNTs@LCMS composite were synthesized by solvothermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$ at 180 °C. The bare LCMS powders are composed of clusters with an average size of 100 nm, which are actually agglomerated by many LCMS nanosheets, as shown in Fig. 1a. When adding CNTs, the LCMS nanosheets grow on the surface of CNTs to form a cable-like nanostructure with favorable dispersion (Fig. 1b). At this mass ratio $(\text{NH}_4)_2\text{MoS}_4$ to CNTs (2.2:1), LCMS nanosheets are uniformly anchored onto the originally smooth CNTs (Fig. S1) without any aggregation in the resulting CNTs@LCMS composite. Fig. 1c shows the TEM image and corresponding fast Fourier transform (FFT) pattern of a typical LCMS nanosheet in LCMS clusters, demonstrating the clear layered structure of MoS_2 and some amorphous component (MoS_3). In the CNTs@LCMS composite, LCMS nanosheets are anchored onto the surface of CNTs, as confirmed by TEM image and corresponding FFT

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