



High-performance MoS₂-based nanocomposite anode prepared by high-energy mechanical milling: The effect of carbonaceous matrix on MoS₂



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ABSTRACT

A MoS₂-based nanocomposite for use as an anode in lithium-ion batteries was prepared via a facile and scalable high-energy mechanical milling (HEMM) technique. In this study, we report the effect of the type of carbon matrix (2D graphite (G), 1D carbon nanotube (CNT), and 0D amorphous carbon (C)) as well as that of the HEMM time on the electrochemical performances. Among all nanocomposites studied, MoS₂/G exhibited the most excellent cycle life, delivering a gravimetric capacity of 737 mAh g⁻¹ after 210 cycles (84% retention) and outstanding rate performance, resulted from a homogenous mixing between MoS₂ and G. In addition, as compared to MoS₂/CNT and MoS₂/C, the capacity retention of MoS₂/G over long-term cycling was markedly steady and stable for various milling times applied. Furthermore, the best weight ratio between MoS₂ and G was experimentally determined to be 7:3 based on the electrochemical performances. The superiority of MoS₂/G was further investigated by density functional theory calculations, which showed the much higher binding energy of G than CNT toward MoS₂, leading to the improved miscibility and the mechanical robustness of MoS₂/G. Overall, the MoS₂/G nanocomposite synthesized by a simple HEMM process presents a new and promising candidate for high-performance anodes for LIBs.

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1. Introduction

Lithium-ion batteries (LIBs) have played a significant role as one of the most promising renewable energy storage devices because of their high gravimetric and volumetric energy, high power density, long cycle life, and low self-discharging property [1–3]. Moreover, the rapidly increasing development of portable devices such as cellular phones, laptops, digital electronics, and electric vehicles necessitates the development of batteries with high capacities, high energy densities, and better cycling stability. To address these issues, much research has been devoted to the development of new materials (or the improvement of traditional materials) as anode

materials for LIBs [4–8]. Currently, graphite is the most popular commercial anode material because it is an abundant and inexpensive natural resource with good cycling stability [9]. However, graphite-based anodes cannot satisfy the increasing demand for high energy densities because of their low theoretical capacity (~372 mAh g⁻¹) and poor rate performance [9–11]. Moreover, the lithium dendrites generated on the surface of graphitic carbon anodes during fast charging processes raise serious safety concerns [12].

Molybdenum disulfide (MoS₂) possesses a layered structure like graphite, with weak van der Waals interactions between individual sandwiched S-Mo-S layers; the spacing between adjacent layers is 6.15 Å, which is significantly larger than that of graphite (3.35 Å) [13]. Therefore, foreign ions (e.g., Li⁺, Na⁺, and Mg²⁺) or molecules can be readily intercalated into MoS₂ without a significant increase in volume. In addition, MoS₂ has attracted a great deal of attention because of its large lithium storage capability (theoretical specific capacity of 670 mAh g⁻¹), resulting from the large number (four

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Li^+) of Li atoms per Mo atom during the conversion reaction [14]. However, the inherent low conductivity and serious volume change of MoS_2 normally are considered as the serious impeding factors for the poor cycling stability and rate property [15].

To address these problems, many recent studies have focused on the synthesis of MoS_2 with different structures or the introduction of nanostructured carbon into MoS_2 using many different approaches, including hydrothermal methods [13,16–20], sonication [11,21], heat treatment [9,22,23], electrospinning [17], microwave irradiation [24], and electrostatic spray deposition [25]. In general, although various MoS_2 structures synthesized using these approaches have demonstrated good results in terms of electrochemical performances, they are more or less complex and difficult to apply widely in industry. More importantly, there have not been many reports that seriously studied the exact role of different carbonaceous matrices for MoS_2 -based LIBs.

Herein, we investigate the MoS_2 /carbon-based nanocomposite anodes synthesized by a convenient and scalable high-energy mechanical milling (HEMM) process. In particular, three different physical types of carbon matrices (2D graphite (G), 1D carbon nanotube (CNT), and 0D amorphous carbon (C)) are considered for the optimal combination with MoS_2 . Although a similar approach has been reported [26], our main focus is on the more appropriate mixing behavior between MoS_2 and carbonaceous material based on their different tribological properties. In fact, both MoS_2 and graphite have been well-known as one of the most representative solid lubricant materials over the past few decades [27–29]. Because of their common properties, when they are under a milling process, a mixing behavior of graphite can be much more efficient than that of other carbonaceous materials. Based on the comparison of the structural characteristics, MoS_2 /G exhibited the most favorable results in terms of mixing properties, which in turn strongly affected the electrochemical performances. It is reported that MoS_2 /G produced under appropriate processing conditions exhibits an excellent rate capability and a high reversible capacity (737 mAh g^{-1} after 210 cycles) that outperforms MoS_2 /CNT and MoS_2 /C. Additionally, the influences of the milling time as well as the weight ratio between MoS_2 and carbon matrix on the MoS_2 -based electrodes are investigated as key parameters for the further improvement of battery performance. The superior performance of MoS_2 /G is based on the homogeneous mixing between MoS_2 and G originated from their physical similarity, which allows a facile electron transport pathway and suppression of particle agglomeration during cycling as analyzed by various characterizations. We further demonstrate the high chemical and electrochemical stability of the MoS_2 /G nanocomposite with a simulation study.

2. Experimental

2.1. Materials

Molybdenum(IV) sulfide ($<2 \mu\text{m}$, 99%, Sigma-Aldrich), multi-walled carbon nanotube (CNT, $>90\%$, Sigma-Aldrich), carbon black-Super PTM (C, 99.99%, Alfa Aesar), and natural graphite powder (G, 200 mesh, 99.9999%, Alfa Aesar) were of analytical grade and used without further purification.

2.2. Material synthesis

Planetary ball milling (Pulverisette 5, Fritsch) was used to synthesize the MoS_2 /carbon nanocomposites at ambient temperature under an Ar atmosphere. MoS_2 powder and the various carbonaceous materials (G, CNT, and C) at mass ratios of 7:3 were placed into a zirconium oxide bowl (80 cm^3) with zirconium oxide balls (diameters $3/8 \text{ in.}$ and $3/16 \text{ in.}$) at a ball-to-powder ratio of 20:1.

HEMM was operated at a rotation speed of 300 rpm with a 30 min break for every hour of milling. For comparison, ball-milled pure MoS_2 was separately prepared without a carbon matrix using the same HEMM conditions. The total milling time was studied at 12, 24, 36, and 48 h for every mixture of MoS_2 and carbon matrix. MoS_2 /carbon nanocomposites with weight ratios of 7:3, 1:1, and 2:1 between MoS_2 and carbon matrix were also prepared to find an optimal mixing ratio.

2.3. Characterization

The crystalline structures of each composite were characterized by X-ray diffraction (XRD, D/MAX-2200 Rigaku, Japan). The morphology and composition were examined by scanning electron microscopy (SEM, Hitachi S4700, Japan) and transmission electron microscopy (TEM, TECNAI G2F30). The specific surface areas were measured by the Brunauer–Emmett–Teller (BET) nitrogen adsorption/desorption method (ASAP 2020, Micromeritics, USA). Raman spectroscopy was performed by a micro Raman spectrometer (ANDOR Monora500i, 633 nm). Thermogravimetric analysis (TGA) was carried out on a SDT Q600 instrument at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air.

2.4. Electrochemical measurements

The as-prepared composites were used to prepare anode electrodes by coating the composites onto copper foil by the doctor blade method using a slurry containing 70 wt% active powder material, 15 wt% carbon black (Super PTM, Aldrich), and 15 wt% poly(vinylidene fluoride) (PVDF, average M_w of 534 000 by GPC, Aldrich) in N-methyl-pyrrolidone (NMP). The samples were then dried overnight at $70 \text{ }^\circ\text{C}$ in a vacuum oven. Coin-type electrochemical cells were assembled in an Ar-filled glove box using lithium foil as the counter electrode, polyethylene (PE) as the separator, and 1 M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 by v/v) as the electrolyte solution. The charge/discharge measurements were carried out galvanostatically over a voltage range of 0.0–3.0 V using a battery cycler (WBCS3000, WonAtech). The rate-cycling performance of the cells was also tested at several different current densities. Electrochemical impedance spectroscopy (EIS) was recorded with an amplitude of 5 mV in the frequency range from 1000 kHz to 1 Hz on a multi-channel electrochemical workstation (ZIVE MP1, WonAtech). The overall specific capacity of MoS_2 -based nanocomposite was calculated based on the total mass of active materials (MoS_2 and carbonaceous matrix). In addition, we separately calculated the capacity contribution from pure MoS_2 and matrix using the following equation.

$$C_{\text{MoS}_2} = C_{\text{MoS}_2/\text{matrix}} \times \text{mass \% of MoS}_2 \quad (1)$$

$$C_{\text{matrix}} = C_{\text{MoS}_2/\text{matrix}} \times \text{mass \% of matrix} \quad (2)$$

where mass % of MoS_2 and matrix was determined from TGA analysis, respectively.

2.5. Simulation details

All density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) with the projector augmented wave (PAW) method [30]. The spin-polarized generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) functional was used to treat the exchange–correlation interaction of the electrons. Local density approximation (LDA) was also employed for comparison. Both

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