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Facile synthesis of MoS_2/graphite intercalated composite with enhanced electrochemical performance for sodium ion battery

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ABSTRACT

MoS_2 is a promising anode material for sodium ion batteries owing to its two-dimensional layered structure and high specific capacity. But it still exhibits a poor cycle stability and limited rate capability for Na^+ storage because of its poor electrical conductivity and structural instability. In this work, MoS_2/graphite composite is fabricated by mechanically delaminated and restacked MoS_2 and graphite to form two-dimensional composite layers. The graphite sheets will improve electrical conductivity and prevent the aggregation as well as structure collapse of the MoS_2 layers during charge–discharge process. The MoS_2/graphite composite exhibits excellent Na^+ storage properties. It delivers a high discharge specific capacity of 358.2 mAh/g at a current density of 100 mA/g in the first discharge process and with capacity retention of 68.1% after 800 cycles (retains 244 mAh/g). The average discharge specific capacities retain 250.9 and 225.4 mAh/g corresponding to the current densities of 100 and 1000 mA/g, showing excellent rate capability. The improved electrochemical performance is attributed to the improved electrical conductivity and structural stability after composition of graphite sheets. The study demonstrates a new research strategy for improving sodium ion storage properties of MoS_2.

1. Introduction

Energy is the foundation of the society that supports the progress of human civilization. As the main energy storage device, lithium ion batteries are key components of portable devices, which are widely used in portable electronics, hybrid electric vehicles, and renewable energy systems [1]. However, lithium-ion batteries are suffering a challenge in large scale energy storage due to limited lithium resources and their high cost. In recent years, sodium ion batteries attracted great interest and is an alternative to lithium ion batteries because of their low-cost and rich resources [2–4]. It is known that sodium and lithium are in the same main group, and many of the properties are very similar. However, the radius of the sodium ions is larger than that of lithium ions; it is difficult to find a suitable electrode material (1.06 Å for Na^+ vs. 0.76 Å for Li^+) [5], which gravely limits the volumetric energy density and rate capacity of sodium ion batteries. Therefore, the study of sodium ion batteries is mainly focused on the development of suitable electrode material to accommodate reversible Na^+ insertion and extraction.

In the past years, many anode materials of sodium ion batteries have been explored, including alloy metals [6–9], carbon materials [10–12], metal oxides/chalcogenides [13–16], and non-metal materials [17–19]. Transition metal dichalcogenides (TMDCs) with analogous structures to graphite have been considered as a novel material for ion insertion/extraction [20]. Among these TMDCs, MoS_2 provides a two-dimensional layered structure and is a promising anode for sodium ion batteries because of its high theoretical capacity (670 mAh/g) [21]. The layer structure of MoS_2 is composed of cyclically arranged Mo and S layers, where Mo is the middle layer, while S is the upper and lower layers. This means that the layer of Mo is sandwiched by two layers of S. The chemical combination between Mo and S atoms is covalent bond, while the adjacent two layers are connected by van der Waals force [22]. In this case, a special interlayered structure with relatively weak interaction and interlayer bonding is formed. Importantly, the weak interaction and interlayer bonding introduced a relatively large interlayer spacing which resulted in a fast and reversible insertion/extraction of sodium ions during faraday reactions [23]. However, MoS_2 still exhibited the poor cyclic stability and rate capability because of the following reasons. Firstly, owing to the attractions of van der Waals in the interlayer, the MoS_2 has an inclination to restack to minimize the surface energy. Secondly, the insertion and extraction of Na^+ resulted in the significant volume change and mechanical stress, which may cause the poor contact between the collector and the active materials, resulting in poor cycling stability [24]. Thirdly, the low intrinsic electronic

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conductivity of MoS_2 procrastinates the rapid electron transfer in electrode reaction.

Several approaches were proposed to overcome these disadvantages, such as compositing, exfoliating, and nanostructuring [4,25–27]. Among these methods, design and fabrication of MoS_2/carbon composites is the most useful way to improve the electrochemical performance of MoS_2 electrode. For example, Tang et al. reported the MoS_2@NHPC composite for sodium ion batteries and showed a high reversible capacity of 500 mAh/g at the current density of 100 mA/g [28]. Shi et al. reported MoS_2–carbon monolayer sandwiched superstructure which can provide a capacity of 477 mAh/g after 200 cycles at 200 mAh/g [29]. However, these approaches are still difficult to large-scale applications because of their high-cost and complicated preparation process. This inspires us to design a facile and low cost process to improve the sodium ion storage properties of MoS_2.

Herein, MoS_2/graphite composite is prepared through a ball milling process, and it is a cheap and productive way to synthesis MoS_2/carbon composite which can meet the requirements for large-scale applications. MoS_2 and graphite are mechanically delaminated and restacked to form a two-dimensional layered structure. The graphite sheets will not only improve electrical conductivity of the composite and accelerate the electron transfer, but also be beneficial to buffer volume variations and prevent the aggregation as well as structure collapse of the MoS_2 layers during charge–discharge process. This means that graphite will improve the rate capability and cycle stability of the MoS_2. Meanwhile, the MoS_2 layers will storage sodium ions and contribution Q2 capacity to the composites. The as-obtained MoS_2/graphite composites show better sodium ion storage properties than pure MoS_2 electrode, including higher rate capability and better cycling stability. This work demonstrates a cheap and productive way to synthesis MoS_2/carbon composite which can meet the requirements for large-scale applications; it will be a new research strategy for improving sodium ion storage properties of MoS_2.

2. Experimental

2.1. Synthesis of MoS_2/graphite composite

MoS_2 (98%) and graphite were both purchased from Sinopharm Chemical Reagent Co. Ltd. MoS_2/graphite powders were prepared by a ball milling method (planetary ball mill; QM-3SP04; Nanjing NanDa Instrument Plant; maximum speed 600 rpm). For the ball milling, MoS_2 and commercial graphite were mixed together with the different weight ratios. The mixing power and milling balls by 1:20 weight ratio were assembled into a hardened steel vial under a glove box filled with argon. The rotation speed of the milling was carried out at 300 rpm for 20 h.

2.2. Characterization

MoS_2/graphite composite was examined by the power X-ray diffraction (XRD) pattern on a Rigaku D/MAX 2400 diffractometer (Japan) with Cu K_α radiation 109 ($\lambda = 1.5418$ Å). The main elements were identified by X-ray photoelectron spectroscopy (XPS, Q3 ESCALAB 250, Thermo VG) and Raman spectra (HR800 JOBINYvon Horiba Raman spectrometer). The microstructures were tested by scanning electron microscopy (SEM, JEOL, JSM-6701F, Japan) and transmission electron microscope (TEM, JEOL, JEM-2010, Japan).

2.3. Electrochemical measurements

In order to display the electrochemical performance, MoS_2/graphite composite was molded into half battery (CR2032) for testing. The preparation process of the electrode is as follows: the active material (MoS_2/graphite composite), conductive agent (acetylene black) and the binder (PVDF) (mass ratio of 8:1:1) were mixed to prepare the slurry. And then the slurry was uniformly coated on a copper foil collector. The electrode pieces were cut into circular electrodes of 14 mm diameter using a slicer and further dried in a vacuum at 120 °C over night, the mass loading of active materials in each electrode can be controlled in the range of 1.2–1.5 mg. The battery was assembled in a glove box with Ar atmosphere. For electrochemical measurement, Na foil was used as the counter and reference electrode, the separator was glass fiber GF/D (Whatman), and the electrolyte was 1 M $NaClO_4$ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed solvent with the weight ratio of 1:1. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical workstation (CHI 660D, Shanghai, China). Discharge–charge measurements were performed on the Land battery testing system (CT2001A). All the tests of battery were conducted in the cut-off voltage range of 0.01–3.00 V.

3. Results and discussion

Fig. 1(a) displays the XRD patterns of MoS_2, graphite, and MoS_2/graphite. The diffraction peaks of the composite match well with that of MoS_2 and graphite. The diffraction peaks of MoS_2/graphite composite located at $2\theta = 14°$, 37°, 44°, 49° and 62° are corresponding to the (0 0 2), (1 0 3), (0 0 6), (1 0 5) and (1 0 7) lattice planes of the pure MoS_2. Compared with the original MoS_2, an excess peak occurs around 27° which could be related to the (1 0 0) plane of the graphite in the MoS_2/graphite composite. Fig. 1(b) displays Raman spectra of MoS_2, graphite, and MoS_2/graphite. For graphite, there are D band and G band of carbon at 1347/cm and 1577/cm, corresponding to sp^3 hybridization for disordered carbon and sp^2 hybridization for graphite,

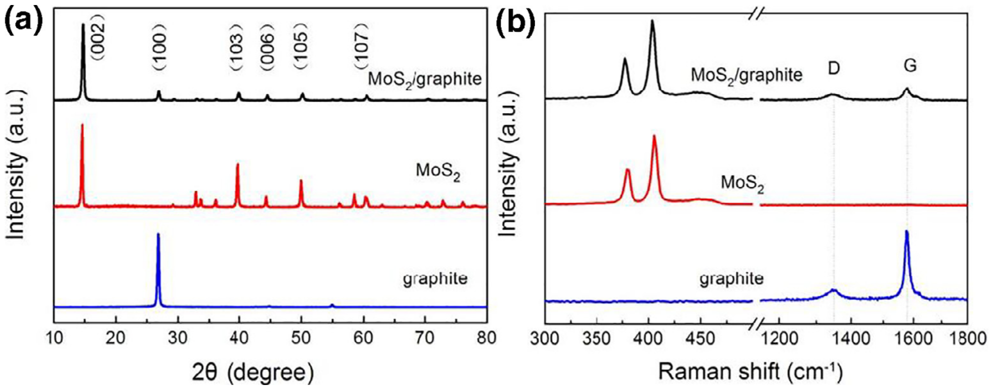

Fig. 1. (a) XRD patterns and (b) Raman spectra of MoS_2, graphite, and MoS_2/graphite.

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