Molybdenum disulfide synthesized by hydrothermal method as anode for lithium rechargeable batteries

GUANGHUI GUO, JIANHE HONG, CHANGJIE CONG, XINWEN ZHOU
Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

KELI ZHANG*
Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China; Centre of Nanoscience and Nanotechnology Research, Wuhan University, Wuhan 430072, People's Republic of China
E-mail: klzhang@whu.edu.cn

The Li-ion rechargeable batteries are considered as the most suitable power sources for portable electronic devices due to their high capacity and energy density and no pollution. They are important energy sources for many portable applications, therefore many researches have been focused on it. The performance of Li-ion rechargeable batteries is under constant improvement. A large part of research is aiming at finding electrode materials with more safety and higher energy densities.

Carbon materials as anode materials for Li-ion rechargeable batteries display excellent cycling stability. However, its theoretical capacity is only 372 mAh/g [1, 2]. In order to overcome these problems, numerous materials have been studied as anodes for lithium ion batteries, such as oxide, nitride and intermetallics whose capacities are comparable or superior to those of graphitized carbon. Molybdenum disulfide with intercalation structure is a good choice because it has a much better performance than other rechargeable batteries, especially for its high energy density and abundant sources in nature.

In the previous work, some molybdenum-based material have also been proposed as anode material of the lithium rocking chair battery, but their study became limited by experiment conditions such as poor stability of the electrolyte at low potential.

In this work, a hydrothermal method at low temperature has been introduced to synthesize the anode materials $MoS_2$and its electrochemical properties have also been discussed.

The starting materials, ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$, elemental sulphur and hydrazine monohydrate (85%), were AR grade. An amount of 2.4 g ammonium molybdate, 0.89 g sulphur and 19.6 ml hydrazine monohydrate were put in Teflon-lined stainless steel autoclaves of capacity 60 ml. The autoclaves were filled with distilled water to 80% of the total volume, then tightly sealed and maintained at 180 °C for 60 hr. After heating, the autoclaves were cooled naturally. The final powder was filtered and washed with water, diluted hydrochloric acid, and ethanol, successively. At last the powder was dried in vacuum at 60 °C for 30 hr. The procedure for the preparation is almost the same as that described in the previous paper [3]. A Shimadzu XRD 6000 diffractmeter with Cu-Kα radiation and an X-ray photoelectron spectrometer with an exciting source Mg-Kα (1235.6 eV) in high vacuum. Moreover, a scanning electron microscope (SEM) was employed for morphological observation and the size of the active materials.

The cell was fabricated using lithium as the anode, MoS_2 powders (80 wt.%) mixed with acetylene black (15 wt.%) and PTFE (5 wt.%) as the cathode, and EC/DEC solution (1:1) containing 1 M $LiPF_6$ as the electrolyte. The cells were cycled between cut-off voltage 0.01 and 2.5 V, at a current density of 100 mA/g.

Fig. 1 shows the binding energies of Mo (3d) and S (2p). The binding energy of M (3d) and S (2p) is 229 eV, 162.1 eV respectively, which are consistent with those of conventional MoS_2. The Mo (3d) and S (2p) peak intensities yield an S/Mo atom ratio of nearly two, element analysis gave the same results as XPS measurements. Fig. 3 shows SEM images for the so-prepared samples, particles tends to agglomerate and uniformly distribute in terms of particle shape, size and texture. The particle size is about 200 nm. An X-ray diffraction pattern of the so-prepared samples is shown in Fig. 2, which indicates the samples should be poorly crystalline MoS_2.

In order to obtain discharge–charge profile of so-prepared MoS_2, the cell was subjected to several cycles at a constant current mode. In the discharge curve an initial open circuit voltage of 2.75 V was observed, which dropped continuously to 0.01 V. During that course there appeared two plateau regions around 1.05 V and 0.52 V, but the following cycles do not show the plateau of 1.05 V, which is due to the formation of solid electrolyte interphase (SEI). The same phenomenon has also been found by L. Fang [4] and Changchun Ai [7]. This result was indicative of the different insertion mechanism of Li ions into MoS_2 between the first and the following cycles.

The cycling performance for the so-prepared MoS_2 powder is shown in Fig. 3. From which, we can observe large irreversible capacity at the first cycle, the

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*Author to whom all correspondence should be addressed.

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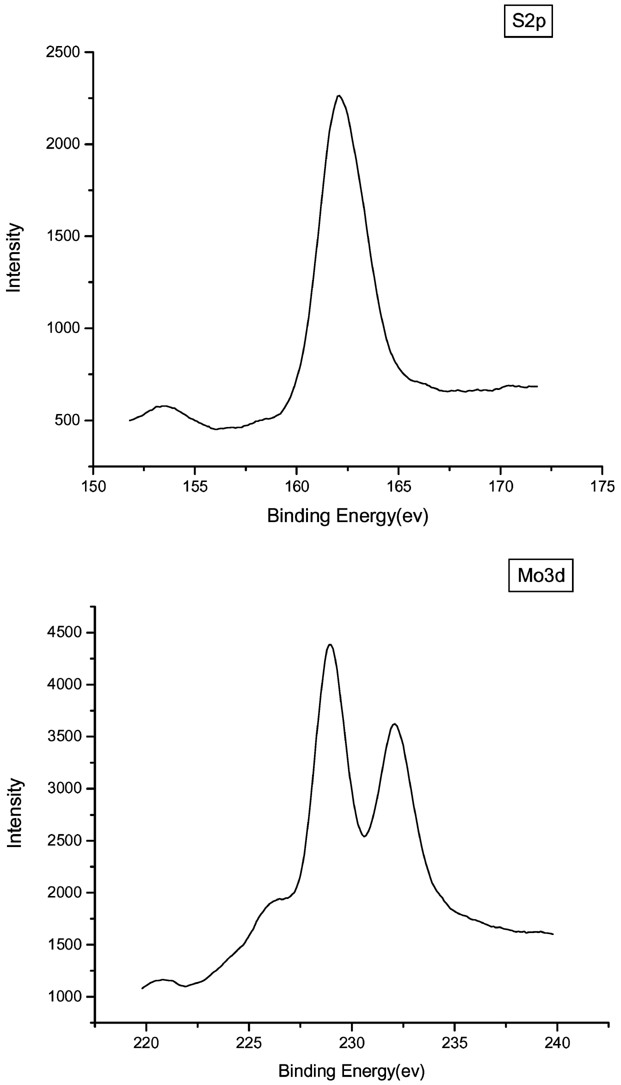

Figure 1 Mo3d and S2p XPS spectra of MoS_2.

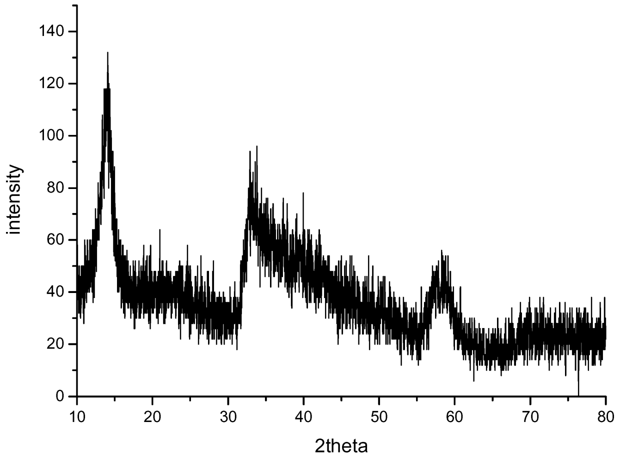

Figure 2 X-ray powder patterns of MoS_2.

discharge capacity of lithium inserted in the first discharge is 1272 mAh/g, which is 3.4 times as large as that of graphite, while the first charge capacity amounts to 801 mAh/g. The first cycle irreversible loss was 37%, which is less than some metal-based composite such as $MnMoO_4$[5], MnV_2O_6[6] and $ZnCo_2O_4$[7]. Even in the 20th cycle, the charge capacity is still more than 400 mAh/g.

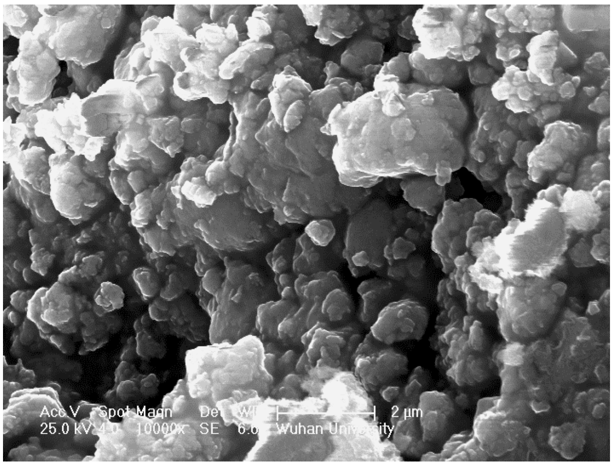

Figure 3 SEM image of MoS_2.

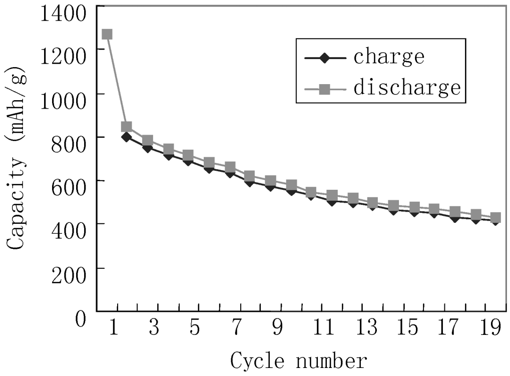

Figure 4 The charge–discharge capacity variation with cycle number of MoS_2/Li test cell.

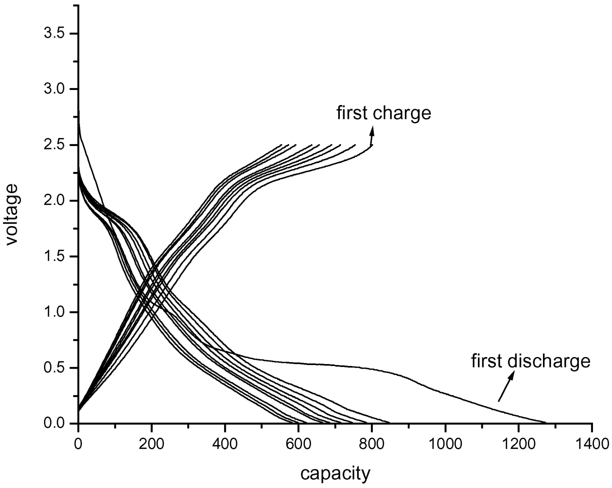

Figure 5 Discharge-charge profile of MoS_2/Li test cell.

According to Moli Energy Limited [8], the fundamental chemistry of this system is the intercalation and de-intercalation of lithium into molybdenum disulfide according to the following equation:

$$x\mathrm{Li} + \mathrm{MoS_2} \leftrightarrow \mathrm{Li}_x\mathrm{MoS_2}$$

We have to consider that the oxidation of molybdenum will decrease till molybdenum exists as Mo[0], which is consistent with the study by X. Rocqefelte of the intercalation compound $LiMoS_2$. He thought that during the intercalation process from MoS_2 to $LiMoS_2$, molybdenum is reduced from an oxidation state IV (d^2) to III (d^3) [9]. From the change in the oxidation state of element molybdenum in the electrode, it is calculated that they can compensate only 4 Li per unit of MoS_2. This compensation for Li ions is not enough to explain the total capacity of the initial discharge, which is 7.6 Li per unit of MoS_2. A similar irreversible capacity has also been discussed by Sung-Soo Kim for the MnV_2O_6 compound [6]. The possible explanations for the missing Li are that some is consumed in the formation of SEI, some alloyed with Mo (further investigations are needed to confirm this speculation), some may be due to the contribution of sulfur, which resembles the role of oxygen in other anode materials such as vanadium oxide materials, acting with lithium leading to the formation of Li-S bond that raises the capacity.

The experiments of the present work show the poorly crystalline MoS_2 powder, synthesized by hydrothermal method, could be a good anode material for lithium ion batteries due to the large electrochemical capacities and the steady potentials versus lithium. Further work is needed to understand the lithium intercalation mechanism underlying it, so as to make it a commercially available material.

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