

Synthesis and Electrochemical Properties of MoO₃

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Abstract: The MoO₃ samples were synthesized by rheological phase-hydrothermal method, and annealed at 450-650°C for 4h. The efforts of different annealed temperatures on the morphologies and electrochemical properties of the final products were systematically investigated. The MoO₃ samples annealed at 550 °C exhibit the best electrochemical properties with a high reversible capability (640 mAh g⁻¹ at current density of 100 mA g⁻¹) and cycling stability (552 mAh g⁻¹ even after 50 cycles), compared with the other samples. These results indicate that the MoO₃ samples could be promising electrode materials for lithium ion batteries.

Introduction

Molybdenum oxides (MoO₂ and MoO₃) received much attention due to their abundant resources, low cost, high electrochemical activity, large capacity (838 mAh g⁻¹ for MoO₂ and 1117 mAh g⁻¹ for MoO₃) for LIBs and environmental friendly nature [1, 2]. Unfortunately, the phase transformation and large volume expansion occur during the Li⁺ intercalation/deintercalation process, leading to the breakdown of electrical pathways, the detachment of the active material from the current collector, and thereafter rapid capacity fading[3, 4].

Recently, several reports have shown that nanocrystals and nanocomposites of metal oxides with much higher surface-to-volume ratios have thus been employed to better accommodate the volume changes for enhancing stability and performance [5]. To achieve MoO₃ nanostructures with various morphologies, a variety of techniques have been developed, for example, chemical vapor deposition, thermal evaporation, sonochemical, electrospinning process, sol-gel, solvothermal, and hydrothermal method. Different approaches have been developed to synthesize nanostructured MoO₃ for LIBs. Lee et al. synthesized MoO₃ nanoparticles using hot filament chemical vapor deposition method (HFCVD) under an argon atmosphere [6]. The corresponding electrochemical performance of LIBs using the nanoparticles exhibits a significant improvement in cycling performance; the reversible capacities of the LIB still remain at 630 mAh g⁻¹ after 150 cycles.

In this paper, we report that the MoO₃ samples were synthesized by rheological phase-hydrothermal method. The electrochemical analysis shows that the MoO₃ electrodes exhibit low initial irreversible capacities, high capacities at different densities and superior cycling performance.

Experimental

Synthesis and characterization of the samples

All chemicals were of analytical grade and were used without further purification. The

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and Hexamethylenetetramine were mechanically mixed in the molar ratio of 1:3 in an agate mortar. After the mixture was ground homogeneously, an appropriate amount of water was added to the powder to obtain a rheological phase state mixture. After treating the above mixture at 140-180 °C for 12 h in a 50 mL Teflon-lined stainless steel autoclave, it was cooled to room temperature. The product was collected, washed with deionized water and absolute ethanol, and dried in air at 80 °C. The precursors were calcined at 550 °C for 4 h under air atmosphere. (designated as MO-1, MO-2, and MO-3, respectively).

Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 molL⁻¹ LiPF₆/ (EC) and (DEC) (1:1). Charge-discharge tests were carried out at different current densities in the range of 1.0 V to 4.6 V.

Results and discussion

The XRD pattern of the final products is depicted in Figure 1. All the diffraction peaks in the XRD pattern can be indexed to the Monoclinic MoO₃, according to the standard XRD data file (JCPDS file no. 85-2405). No peaks of impurities can be detected from the XRD pattern.

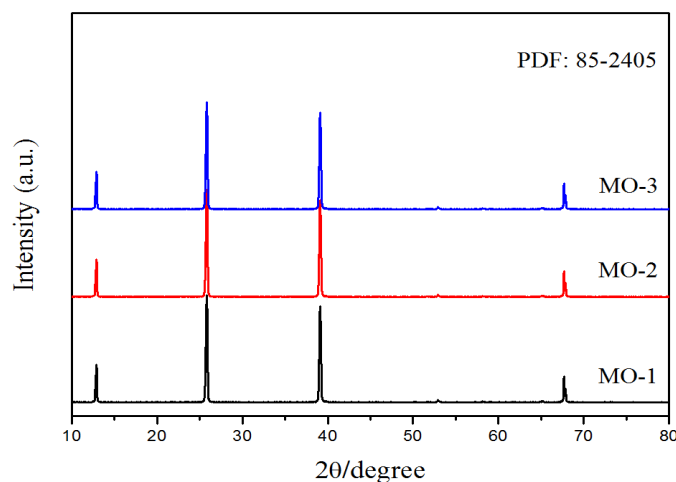


Fig. 1. XRD patterns of the three MoO₃ samples.

The surface morphological features of the samples were investigated by SEM in Fig.2. The products MO-1 sample display a micro-rods structure without aggregation. It is well known that the particle size, particle size distribution and morphologies of the other samples(MO-2 and MO-3) will directly influence the electrochemical performance of the electrode materials. Considering their micro-sheets structures favoring the diffusion of Li⁺ ions and electrode–electrolyte contacts during the electrochemical reaction, the MoO₃ samples are expected to improve the electrochemical performance.

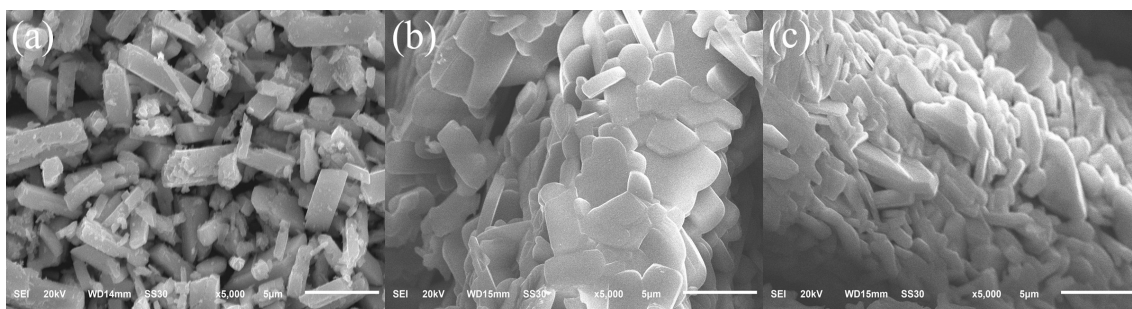


Fig. 2. SEM images of (a) MO-1, (b) MO-2, and (c) MO-3.

The electrochemical performances of the MoO_3 samples were measured via coin cell testing. Fig. 3 illustrates the discharge–charge profiles of the MoO_3 samples as anode materials for rechargeable lithium batteries at a current density of 100 mA g^{-1} at room temperature in a potential window between 0.01 and 3.0 V (versus Li^+/Li). From these, a large irreversible capacity at the first cycle is observed. The specific capacity of the MO-1 and MO-3 showed an obvious decrease with cycling, from 811 and 889 mAh g^{-1} for the first cycle to 397 and 463 mAh g^{-1} for the 50th cycle, whereas MO-2 exhibits the best performance for Li^+ insertion, the MO-2 delivers a larger initial capacity of 801 mAh/g and shows a high reversible capacity of 552 mAh g^{-1} for the second cycle, which is much higher than what was reported for those samples. The excess capacities could be associated with the decomposition of the electrolyte at low voltages generating a solid electrolyte interphase (SEI) layer and the further lithium storage by interfacial charging at the metal/ Li_2O interface. It is obvious that the MO-2 electrode shows much improved cycling performance with higher specific capacities at the same cycle with the same current density, as compared with the other samples, which may be attributed its bigger porous structure.

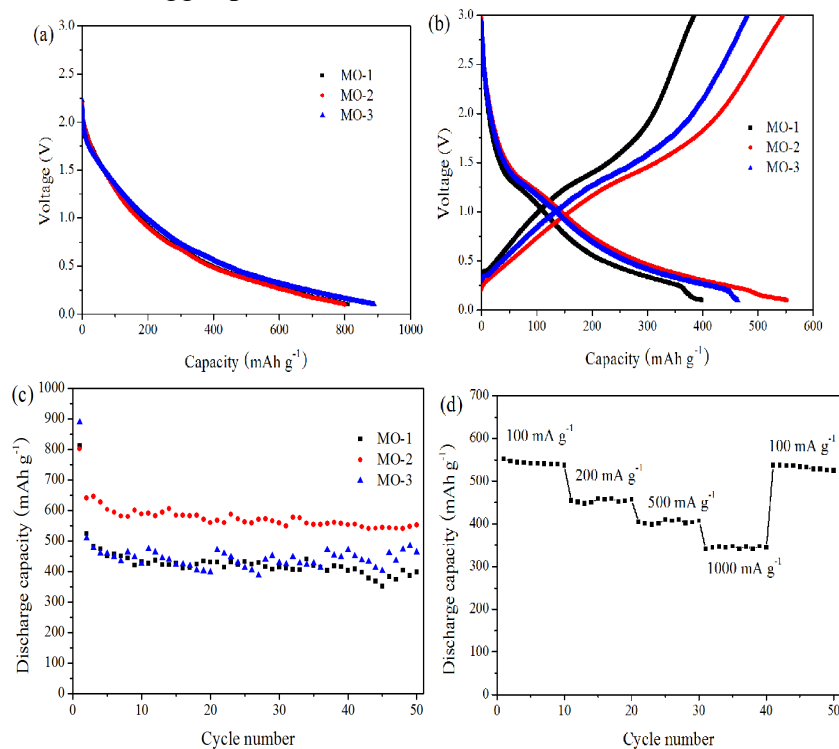


Fig. 3. (a) the first, (b) 50th discharge/charge curves and (c) cycling performance of the MO-1, MO-2, and MO-3; (d) cycling performance of the MO-2 electrode at various current densities.

To better understand the electrochemical behavior of the MO-2 electrode, we also investigated its rate performance as shown in Fig.3d. The cell shows good rate capability with average discharge capacity of 550, 454, 404, and 341 mAh g⁻¹ when the current density increased stepwise to 100, 200, 500, and 1000 mA g⁻¹, respectively. Upon altering the current density back to 100 mA g⁻¹, an average discharge capacity as high as 537 mAh/g could be recovered. These results demonstrate that the MO-2 electrode has great potential as high-rate anode material in lithium-ion batteries.

Conclusion

In summary, we have shown that the MoO₃ electrodes were synthesized via rheological phase-hydrothermal method, annealed at 550 °C for 4h. When used as an anode material for LIBs, the as-prepared the MoO₃ electrodes show a high specific discharge capacity, superior rate capability, and excellent cycling stability. The MO-2 electrode behaved an initial capacity of 801 mAh g⁻¹ at a current density of 100 mA g⁻¹. After 50 cycles, the sample still retained a high capacity of 552 mAh g⁻¹. Particularly, when the current density was increased to 500 mA g⁻¹, the reversible capacity of anode still arrived at 404 mAh g⁻¹. The improved electrochemical performance enables such the MoO₃ electrodes to be a promising anode material for next-generation, high-power lithium-ion batteries.

Acknowledgements

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