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Hierarchical NiMoO₄ nanowire as an anode material for lithium ion batteries

Jinsong Chen, Rongfei Zhao, Ting Wang, Lin Li*, Qing Liu

Key Laboratory of Functional Materials and Chemistry for Performance and Resource of Guizhou Education Department, Anshun University, Anshun 561000, China

*Corresponding author e-mail: 496063041@qq.com

Abstract. The NiMoO₄ samples were synthesized by rheological phase-hydrothermal method. The efforts of different annealed temperatures on the morphologies and electrochemical properties of the final products were systematically investigated. The NiMoO₄ samples exhibit the best electrochemical properties with a high reversible capability (640 mAh g⁻¹ at current density of 50 mA g⁻¹) and cycling stability, compared with the other samples. These results indicate that the NiMoO₄ samples could be promising electrode materials for lithium ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) is a fast-developing technology in electric energy storage, are the dominant power source for a wide range of the communications, transportation and renewable-energy sectors [1]. The current choice of anode materials for LIBs is graphite due to its long cycle life, abundant material supply and relatively low cost. However, graphite, the anode material currently used in commercial LIBs, has a relatively low Li storage capacity of 370 mAh g⁻¹[2].

Recently, many metal molybdates with different morphologies and sizes have been made via the hydrothermal approach to investigate their crystal growth mechanisms or physical properties. The lithium storage capabilities of molybdates have also received little attention. Transition metal molybdates, especially NiMoO₄, have gradually been considered as promising effective and scalable alternatives to the commercial graphite anode for LIBs in view of their excellent electrochemical performance, low-cost, environment benignity and abundance [3, 4]. Most importantly, NiMoO₄ has been reported to demonstrate better performance than single-component metal oxides due to its multiple feasible oxidation states, large cell parameters and comparative higher electrical conductivity (10⁻⁶ S cm⁻¹)[5, 6].

In this paper, we report that the NiMoO₄ nanorod were synthesized by hydrothermal method. The electrochemical analysis shows that the NiMoO₄ nanorod exhibit low initial irreversible capacities, high capacities at different densities and superior cycling performance.

2. Experimental

2.1. Synthesis and characterization of the samples

All chemicals were of analytical grade and were used without further purification. In a typical experiment, 3 mmol of NiCl₂ · 6H₂O and 3 mmol of Na₂MoO₄ · 7H₂O were dissolved successively in 40



mL deionized water with magnetic stirring at room temperature. After treating the above mixture at 180 °C for 12 (6 and 9) 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. (Designated as NMO-1, NMO-2, and NMO-3, respectively).

2.2. Characterization

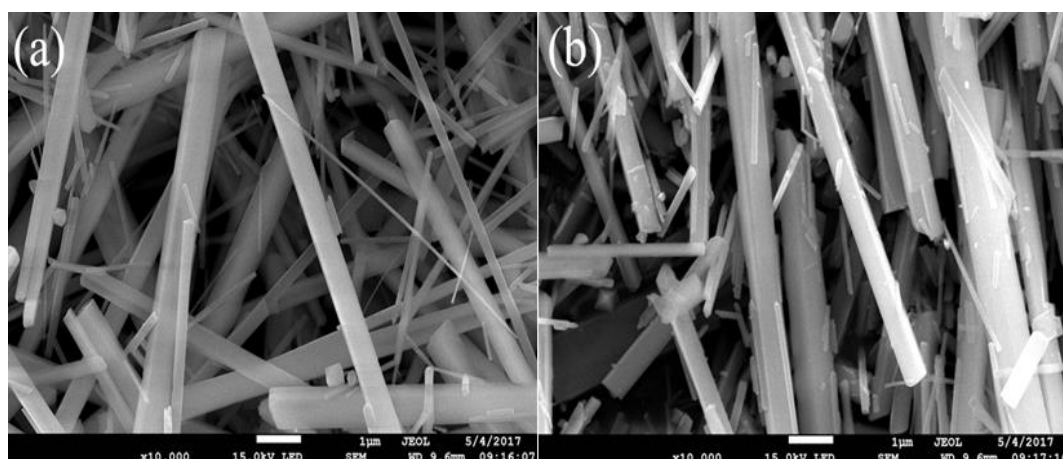
Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

2.3. Electrochemical measurement

The electrochemical properties of the products were measured via a model test cell system. The working electrodes were prepared by compressing a mixture of as-obtained (70 wt %), acetylene black (250 wt %) and polytetrafluoroethylene (PTFE) (10 wt %) onto a copper foil. Then the coated electrodes were dried at 110 °C for 24 h in a vacuum furnace. The counter and reference electrodes were Li foil. Between the anode and cathode, there was the electrolyte which was 1 M LiPF₆ dissolved in a 50/50 vol % mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The separator was Celgard 2400 porous polypropylene. The counter and reference electrodes were lithium foil. The model test cells were assembled in an argon-filled glove box. Charge-discharge tests were carried out at different current densities in the range of 0.01 to 3.0 V. Cyclic voltammetry (CV) tests were carried out in the potential window of 0.01 to 3.0 V on an electrochemical workstation (CHI 660). Electrochemical impedance spectroscopy (EIS) experiments were conducted in the frequency range of 0.01-100 kHz on a CHI 600A electrochemical analyzer.

3. Results and discussion

The surface morphological features of the samples were investigated by SEM in Fig.1. The products NMO-3 sample display a nanorods structure without aggregation. It is well known that the particle size, particle size distribution and morphologies of the other samples (NMO-1 and NMO-2) 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, NiMoO₄ samples are expected to improve the electrochemical performance.



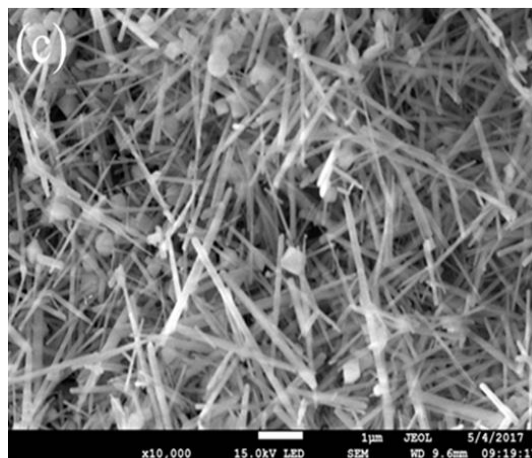


Figure 1. SEM images of (a) NMO-1, (b) NMO-2, and (c) NMO-3.

The XRD pattern of the NMO-3 samples is depicted in Fig.2. All the diffraction peaks in the XRD pattern can be indexed to the monoclinic NiMoO_4 , according to the standard XRD data file (JCPDS file no. 86-0361). No peaks of impurities can be detected from the XRD pattern.

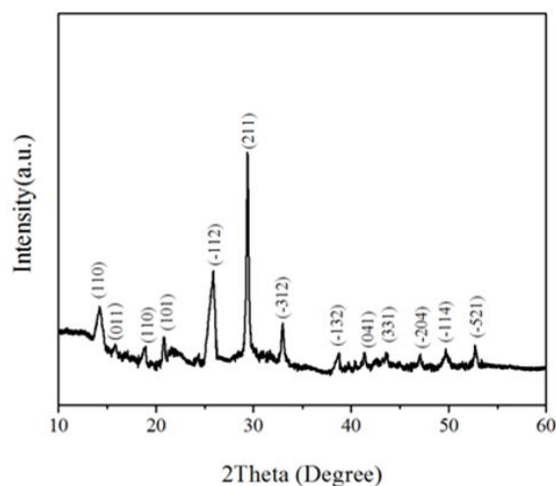


Figure 2. XRD patterns of the NMO-3 samples.

The electrochemical performances of the NiMoO_4 samples were measured via coin cell testing. Fig. 3 displays the initial five consecutive CV curves of NMO-3 electrode at a scan rate of 0.1 mV s^{-1} in the voltage window of 0.01-3.0 V. It is clear from the CV curves that there is substantial difference between the first and subsequent cycles. In the first cycle, there are two obvious irreversible reduction broad peaks at 0.33 and 1.09 V. The first anodic scan shows two peaks at 1.38 and 1.7 V which correspond to the oxidation of metallic Ni and Mo to Ni^{2+} and Mo^{6+} , respectively. In the second and subsequent cycles, two cathodic peaks located at 0.33 and 1.09 V are shifted to 0.58 and 1.39 V.

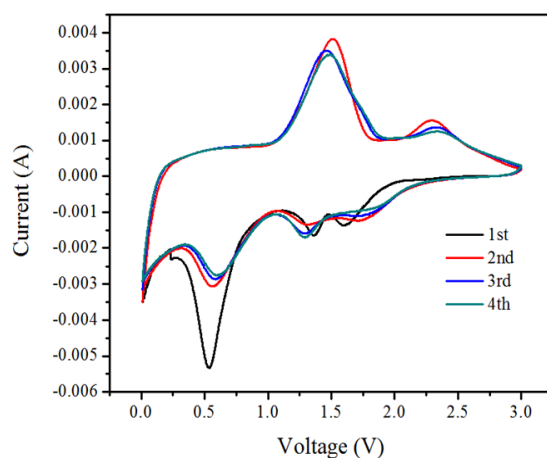


Figure 3. (a) Cyclic voltammograms profiles of NMO-3.

Fig. 4 illustrates the discharge–charge profiles of the NiMoO_4 samples as anode materials for rechargeable lithium batteries at a current density of 100 mA g^{-1} in a potential window between 0.01 and 3.0 V (versus Li^+/Li). The specific capacity of the NMO-1 and NMO-2 showed an obvious decrease with cycling, from 1143 and 1386 mAh g^{-1} for the first cycle to 257 and 223 mAh g^{-1} for the 50th cycle, whereas the NMO-3 delivers a larger initial capacity of 1308 mAh/g and shows a high reversible capacity of 421 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 NMO-3 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.

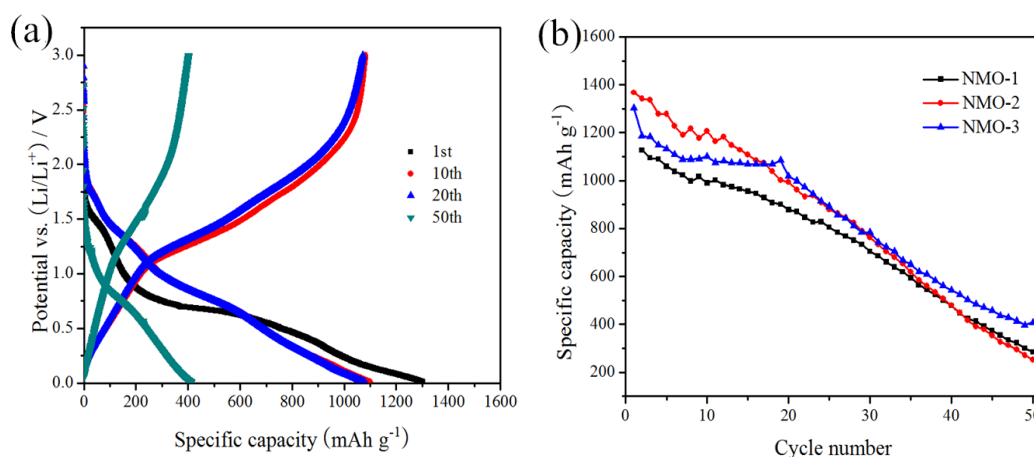


Figure 4. (a) Galvanostatic charge-discharge voltage profiles of NMO-3; (b) Cycling performance of the NMO-1, NMO-2, and NMO-3.

To better understand the electrochemical behavior of the NMO-3 electrode, we also investigated its rate performance as shown in Fig.5. The cell shows good rate capability with average discharge capacity of 1338, 905, 807, and 231 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 576 mAh g^{-1} could be recovered. These results demonstrate that the NMO-3 electrode has great potential as high-rate anode material in lithium-ion batteries.

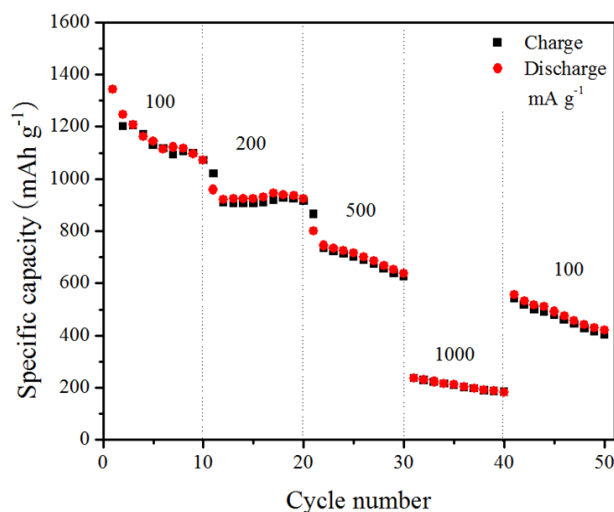


Fig. 5. Cycling performance of the NMO-3 electrode at various current densities.

4. Conclusion

In summary, we have shown that the NiMoO_4 electrodes were synthesized via rheological phase-hydrothermal method. When used as an anode material for LIBs, the as-prepared the NiMoO_4 electrodes show a high specific discharge capacity, superior rate capability, and excellent cycling stability. The NMO-3 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 NiMoO_4 electrodes to be a promising anode material for next-generation, high-power lithium-ion batteries.

Acknowledgements

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