

Fe₂(MoO₄)₃ microspheres as a potential anode material for lithium ion batteries

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Abstract: Fe₂(MoO₄)₃ microspheres are fabricated by a facile hydrothermal process assembled from Fe₂(MoO₄)₃ nanoplates. The microstructures and morphologies of the Fe₂(MoO₄)₃ nanorods was characterized using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The discharge capacity of Fe₂(MoO₄)₃ microspheres show a larger initial capacity of 1169 mAh/g and still retains a high capacity of 670 mAh/g, even after 80 cycles. More importantly, when the current density increased to 500 mA/g, it can render reversible capacity of 449 mAh/g even after 50 cycles, indicating its potential applications for next-generation high power lithium ion batteries (LIBs).

Introduction

Most previous approaches to obtain molybdates or tungstates need high temperature and harsh reaction conditions ^[1-3], such as solid-state reaction ^[4], sol-gel method ^[5], hydrothermal synthesis, self-templated methods, microwave-assisted solution synthesis, etc. For example, FeMoO₄ hollow microspheres with good photocatalytic activity via a template-free hydrothermal method ^[6]. The lithium storage capabilities of molybdates have received little attention. Most works have focused on their possible applications as anode materials, and their possible applications as cathode materials still remain largely unexplored. For example, Leyzerovich et al. ^[7] introduced NiMoO₄ as an anode material in lithium ion batteries in 2004. It is proposed that such a high capacity is related to many vacancies in the structure of NiMoO₄ nanorod bundles, in which Li⁺ ion could be reversibly incorporated. Haetge et al. ^[8] have reported nanocrystalline nickel molybdate (NiMoO₄) thin film electrodes with a 3D honeycomb structure were successfully produced through facile polymer templating strategies. The initial discharge capacity is 270 mA/hg at a rate of 1.4 C within a potential window of 3.5–1.5 V vs. Li/Li⁺. Recently, Zheng et al. ^[9] have reported 3D flowerlike Fe₂(MoO₄)₃ micron-spheres were hydrothermal process with FeCl₃·7H₂O and Na₂MoO₄ as raw materials. The 3D flowerlike Fe₂(MoO₄)₃ micron-spheres synthesized at 160 °C exhibit the best electrochemical properties with a larger initial capacity of 1431 mAh/g at a current density of 100 mA/g, and cycling stability (747 mAh g⁻¹ even after 50 cycles).

Herein, we report the electrochemical properties of Fe₂(MoO₄)₃ as anode material in lithium ion batteries. Fe₂(MoO₄)₃ microspheres assembled from nanoplates were synthesized via a hydrothermal process. The possibility of using these materials as cathode material for lithium ion batteries.

Experimental

Synthesis and characterization of the samples. All chemicals were of analytical grade and were used without further purification. In a typical synthesis, 1.0 mL dilute HCl was added dropwise in 15 ml 0.08 M aqueous FeCl₃·7H₂O solution. Then, 15 ml 0.12 M aqueous Na₂MoO₄ solution was added under magnetic stirring at room temperature. After 5 min of stirring, the resulting mixture was transferred to a 50 mL Teflon-lined stainless autoclave, which was sealed and maintained at 180 °C for 24 h in an electrical oven. The autoclave was cooled to room temperature

naturally. The products were collected by centrifugation, washed several times with distilled water and absolute ethanol and finally dried at 60°C for 12 h.

The crystallinity and structure of the samples were characterized by X-ray diffraction (XRD), using a Philips X-ray diffractometer with Cu K α radiation ($\lambda = 1.5405\text{\AA}$), recorded with 2θ ranging from 10° to 50°. The morphologies of the samples were observed using a scan electron microscopy (SEM) images and EDS were carried out with a LEO 1530VP (LEO, Germany) electron microscopy.

Electrochemical measurements. Electrochemical performances of the products were tested in a model test cell system. Positive electrodes were prepared by pressing the mixtures of the active material (70%), acetylene black (20%), and polytetrafluoroethylene (PTFE) (10%) onto a nickel grid. Prior to being used, the positive electrodes were dried at 125°C in a vacuum furnace for 24 h. The electrolyte was a solution of 1 M LiPF₆/ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). 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 dry box. Charge-discharge tests were carried out at different current densities in the range of 0.01 V to 3.0 V.

Results and discussion

Fig. 1 depicts the XRD pattern of the Fe₂(MoO₄)₃ microspheres. All the reflection peaks could be indexed to monoclinic Fe₂(MoO₄)₃ with calculated lattice constants of $a = 15.72\text{\AA}$, $b = 9.24\text{\AA}$, and $c = 18.22\text{\AA}$, which is in good agreement with the literature values (JCPDS file Card No. 35-0183)^[10]. No other impurity peak is detected.

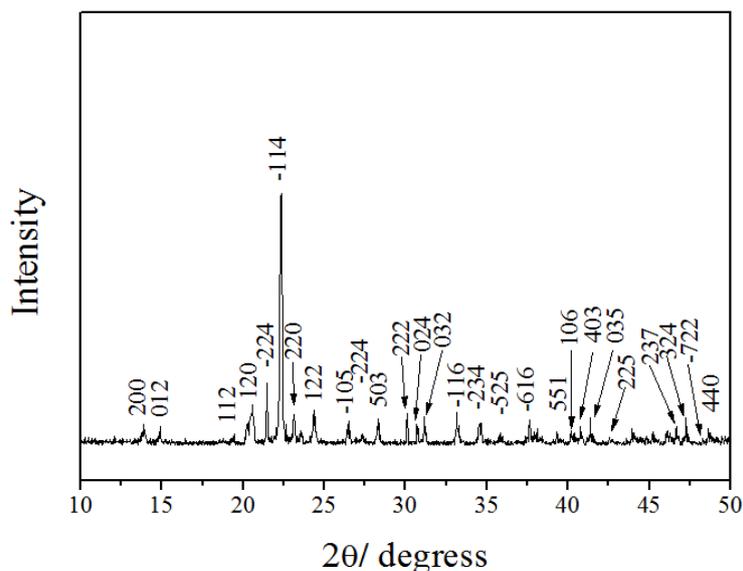


Fig. 1. XRD patterns of the Fe₂(MoO₄)₃.

Fig. 2 shows the SEM images of the Fe₂(MoO₄)₃ microspheres sample. The overall morphology of the samples, as shown in Fig. 2a, indicates that large scale microspheres were achieved by using this simple hydrothermal approach. The high magnification SEM image (Fig. 2b and c) shows that the microspheres have diameters ranging from 5 to 20 μm , and each of the nanoplates consists of a large number of primary grains with submicron size. The chemical composition analysis in Fig.2d, indicates that the Fe₂(MoO₄)₃ microspheres are made of Fe, Mo and O and the molar ratio of Fe to Mo and O is approximately equal to 1: 1.4: 5.8. The carbon peak originates from the surrounding carbon matrix. The Cu peaks originate from the carbon-coated Cu grid used as a sample support during SEM measurements. Taking into account the error of the measurement, the chemical formula is close to Fe₂(MoO₄)₃.

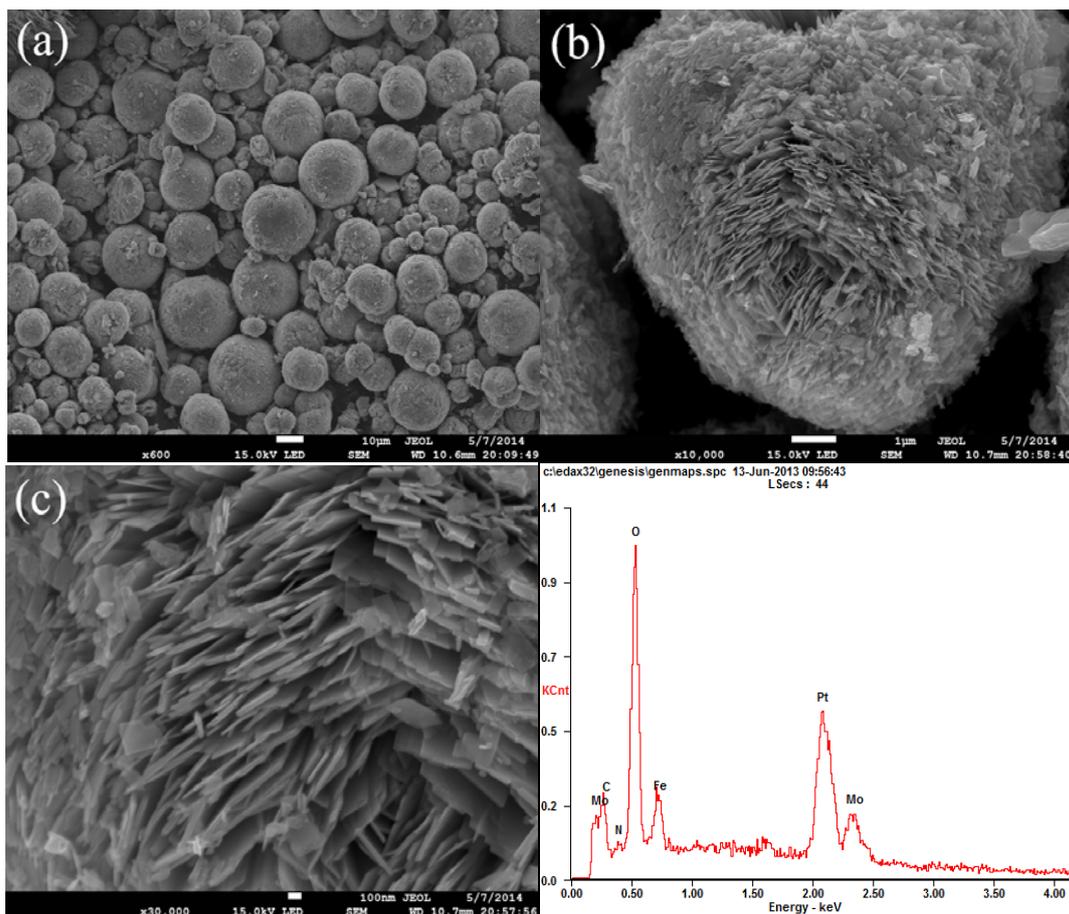


Fig. 2. SEM patterns and EDS patterns of the $\text{Fe}_2(\text{MoO}_4)_3$.

The electrochemical performances of $\text{Fe}_2(\text{MoO}_4)_3$ were measured via coin cell testing. Fig.3(a, b) showed the typical discharge/charge cycles of the as-prepared $\text{Fe}_2(\text{MoO}_4)_3$ electrodes cycled between 0.01 and 3.0 V with a current density of 100 mA/g at room temperature, respectively. One can see immediately the difference between the first and following cycles. In the first discharge curves, two voltage plateaus near at 1.6 and 0.6 V is clearly observed in all samples, and the peak remains to higher potential at 0.6 V in the following cycles. While the charge curves of the three samples show a de-insertion plateaus at about ~1.5 V. The initial discharge capacity of the $\text{Fe}_2(\text{MoO}_4)_3$ was 1169 mAh/g and shows a high reversible capacity of 948 mAh/g for the second cycle. It still retains a high capacity of 670 mAh/g, even after 85 cycles.

To good understand the electrochemical behavior of the $\text{Fe}_2(\text{MoO}_4)_3$ microspheres, we also investigated its rate performance, as shown in Fig 3(c, d). The $\text{Fe}_2(\text{MoO}_4)_3$ electrode is cycled at various current densities (100–1000 mA/g). The cell shows good rate capability with average discharge capacity of 785, 486, 449, and 299 mAh/g when the current densities are 100, 200, 500, and 1000 mA/g, respectively. Upon altering the current density back to 100 mA/g after the rate performance testing, an average discharge capacity as high as 811 mAh/g could be recovered. Large surface area and the short diffusion length of spherical porous structured electrode can improve the kinetic properties of the lithium-ion during intercalation and easily delivers high discharge capacity even under extremely high currents. These results demonstrate that the $\text{Fe}_2(\text{MoO}_4)_3$ microspheres have great potential as high-rate anode material in LIBs.

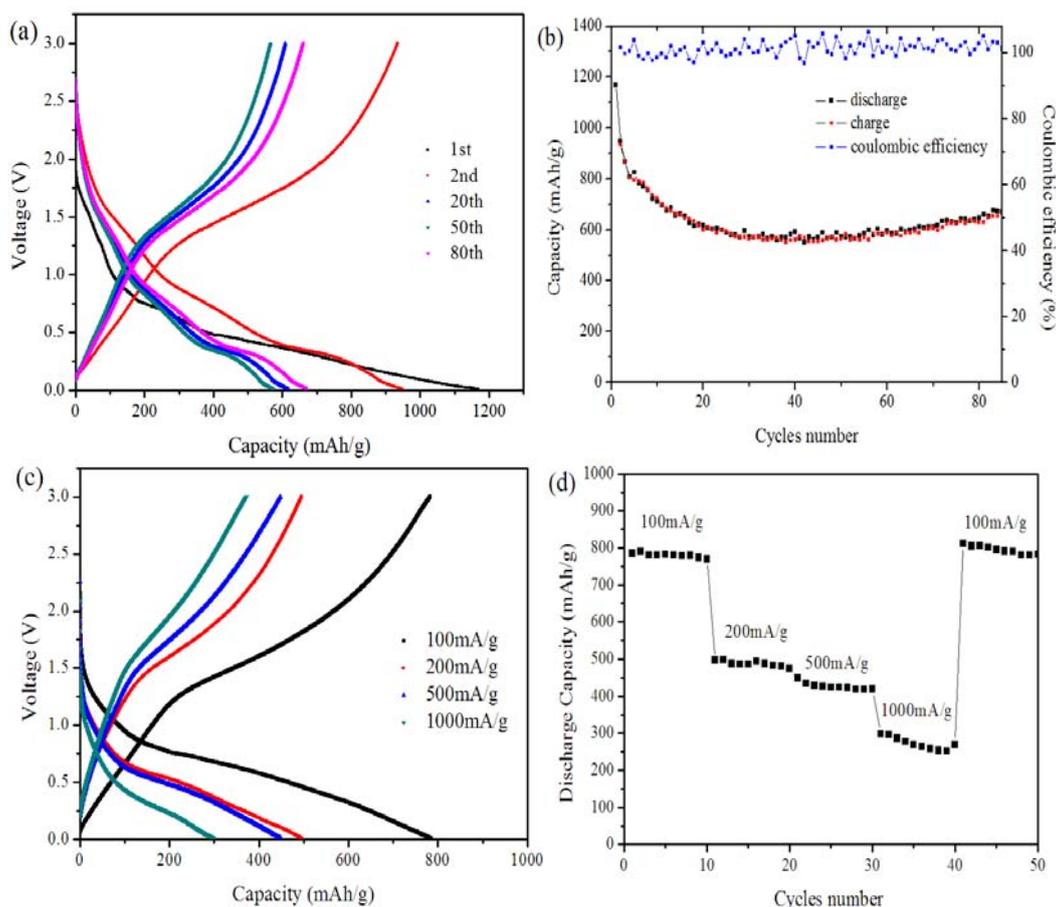


Fig. 3. Typical discharge/charge curves (a) and Cycling performance (b) of the $\text{Fe}_2(\text{MoO}_4)_3$; the first discharge/charge curves (c) and cycling performance(d) of the $\text{Fe}_2(\text{MoO}_4)_3$ electrode at various current densities

Summary

In summary, we have shown that $\text{Fe}_2(\text{MoO}_4)_3$ electrodes can be produced with a $\text{Fe}_2(\text{MoO}_4)_3$ microspheres assembled from nanoplates were synthesized via a hydrothermal process. These materials exhibit enhanced lithium ion storage capabilities, because the combination of nanoscale porosity and nanocrystallinity seems to provide a beneficial microstructure for battery applications.

Acknowledgments

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References

- [1] J. Chen, F.Y. Cheng, Combination of lightweight elements and nanostructured materials for batteries. *Acc. Chem. Res.* 42 (2009) 713-723.
- [2] Y.S. Luo, W.D. Zhang, X.J. Dai, Y. Yang, S.Y. Fu, Facile synthesis and luminescent properties of novel flowerlike BaMoO_4 nanostructures by a simple hydrothermal route. *J. Phys. Chem. B*, 113 (2009) 4856-4861.
- [3] Hyde, B. G.; Andersson, S.; *Inorganic Crystal Structure.*; Wiley: New York, 1989.
- [4] H.E. Swanson, M.C. Morris, R.P. Stinchfield, E.H. Evans, Standard X-ray diffraction powder patterns, NBS Monogr. (U.S.) 25 (1963) 24-27.

- [5] M. Bonanni, L. Spanhel, M. Lerch, E. Fuglein, G. Muller, Conversion of Colloidal ZnO–WO₃ Heteroaggregates into Strongly Blue Luminescing ZnWO₄ Xerogels and Films, *Chem. Mater.* 10 (1998) 304-310.
- [6] J.X. Cui, W.S. Wang, L. Zhen, W.Z. Shao, Z.L. Chen, Formation of FeMoO₄ hollow microspheres via a chemical conversion-induced Ostwald ripening process, *CrystEngComm.* 14 (2012) 7025-7030.
- [7] N.N. Leyzerovich, K.G. Bramnik, T. Buhrmester, H. Ehrenberg, H. Fuess, Electrochemical intercalation of lithium in ternary metal molybdates MMoO₄ (M: Cu, Zn, Ni, and Fe), *J. Power Sources.* 127 (2004) 76-84.
- [8] J. Haetge, I. Djerdj, T. Brezesinski, Nanocrystalline NiMoO₄ with an ordered mesoporous morphology as potential material for rechargeable thin film lithium batteries, *Chem. Commun.* 48 (2012) 6726-6728.
- [9] Hao Zheng, Lin Li, Hong Gao, Qing Zhang, Shiquan Wang, Chuanqi Feng, 3D flower-like Fe₂(MoO₄)₃ micron-spheres: Synthesis and Applications in lithium-ion batteries, *CHINESE J INORG CHEM.* 30 (2014) 2761-2766.
- [10] T.H. Kim, B. Ramachandra, J.S. Choi, M.B. Saidutta, K.Y. Choo, S.D. Song, Y.W. Rhee, Selective oxidation of methanol to formaldehyde using modified iron-molybdate catalysts, *Catal. Lett.* 98 (2004) 161-165.