Fabrication of Novel Vanadium Dioxide Nanorods as Cathode Material for Rechargeable Lithium Batteries

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Novel vanadium dioxide nanorods in diameter of 40–60 nm and in length up to 1–2 μm were successfully fabricated via a surfactant-assisted hydrothermal method at 180 °C for 48 h. Electrochemical test results demonstrated that the nanorods showed an initial discharge specific capacity of 306 and 245 mAh/g in the fifteenth cycle.

Among numerous transition metal oxides, vanadium oxides are especially interesting because vanadium forms a diverse binary oxides with the general formula VO_{2+x} in addition to the well-known phase V_2O_5 and V_2O_3, including VO_2, V_6O_{13}, V_4O_9, and V_3O_7. The structures of these phases are built up of distorted VO_6 octahedra that share both corners and edges.[1] They can be described as share corners in the hypothetical VO_3 as in ABO_3 perovskites. VO_2(B) ((B) means a kind of crystal phase B, the same as (M) and (R) hereinafter) was found to have better electrochemical[2] performance compared to the well-known binary oxide V_2O_5, which could be attributed to a structure stability arising from an increased edge sharing and the consequent resistance to lattice shearing during cycling and a lower cell potential which is advantageous to electrolyte oxidation.

It is well known that many chemical and physical properties of materials are dependent, to a large extent, on both initial particle size and the manner they organized. Therefore, controlling the dimension and shape of materials at the mesoscopic level is one of the most challenging issues presently faced by synthetic scientists. Over the past decades, there has been a continuity interest in coaxing starting particles into desired nanostructures, such as nanotubes, nanorods, nanowires, and nanoribbons.[3] Of date, various one-dimensional (1D) nanostructured vanadium oxides have been prepared successfully, such as vanadium oxide nanotubes,[4] vanadium pentoxide nanorods and nanowires,[5] and VO_2(R) nanorods.[6] However, there are few reports for the synthesis of 1D nanostructure of VO_2(B). Since VO_2(B) is metastable[7] and it tends to transform to thermodynamically more stable VO_2(R) which is not an attractive cathode when the temperature is higher than 300 °C, it is difficult to be synthesized via high temperature procedures. In the present work, fabrication of novel VO_2(B) nanorods was carried out via a surfactant-assisted hydrothermal method and electrochemical experiments were run in order to show the charge/discharge capacity of the as-synthesized novel nanorods.

All chemicals were analytical grade and used without further purification. In a typical procedure, 10 mmol V_2O_5 and 10 mmol cetyltrimethylammonium bromide (CTAB) was added into a Teflon-lined autoclave of 40-mL capacity and filled with distilled water to 90% capacity, then sealed and maintained at 180 °C for 48 h. After the reaction was completed, the result black solid product was collected and washed with absolute ethanol and distilled water several times to remove possibly remaining in the final products, and finally dried at 80 °C for 6 h.

The over all crystallinity and purity of the as-synthesized samples were examined by X-ray powder diffraction (XRD) using a D/MAX-III diffraction with Cu Kα radiation ($\lambda = 0.15418$ nm). The size distribution and morphology of the nanorods were analyzed on a JEOL-2010 high-resolution transmission electron microscopy (HRTEM) with an accelerating voltage of 200 kV. Electrochemical test was performed in cell with metallic lithium as the negative electrode. The electrolyte was $LiPF_6$ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50), Celgard 2400 as separators. The positive electrode composites were made by mixing the nanorods, acetylene black and poly(tetrafluoroethylene) (PTFE) (60:30:10). All cells used in this study were assembled in an argon-filled dry box. Charge-discharge tests were carried out at a constant current density of 0.4 mA/cm^2.

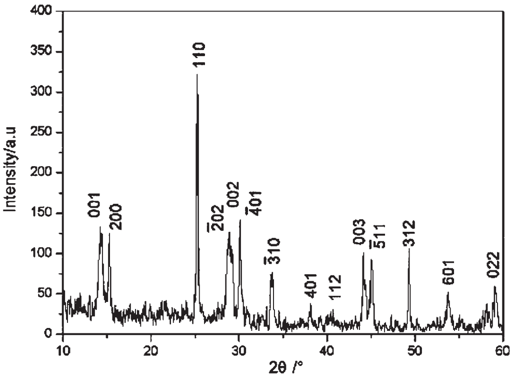

Figure 1. XRD pattern of as-synthesized VO_2(B) nanorods.

Figure 1 displays the XRD pattern of the obtained samples. All the peaks can be rapidly indexed to VO_2(B) phase consistent with the standard value of JCPDS 31-1438 ($C2/m$, $a = 1.203$, $b = 0.3693$, $c = 0.642$ nm, $\beta = 106.6°$). In addition, it was found that peak (110) is the only peak that gains a substantial increase in relative intensity, which may be caused by the orientation growth of VO_2(B). No impurity phases such as V_2O_5, VO_2(R), and VO_2(M) are detected from the XRD pattern, indicating that VO_2(B) nanorods with high purity could be obtained under the current synthetic conditions.

The final products consist mainly of vanadium dioxide nanorods. Figure 2a displays that the sample is rod-like structure with diameters 40–60 nm and length 1–2 μm, and aspect ratios lie in the range of 25–40. The structure of VO_2(B) nanorods is further examined by HRTEM. The lattice image together with corresponding fast Fourier transformation (FFT) is shown in

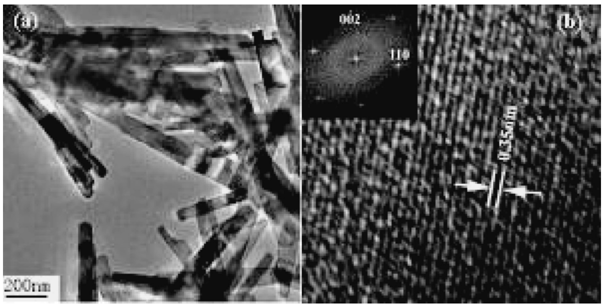

Figure 2. (a) TEM image showing the rod-like morphology of B phase VO_2. (b) HRTEM image of an individual nanorod. The imaged lattice spacing amounts to 0.35 nm corresponding to the (110) plane of B phase. The inset at the left top is the corresponding FFT of the image.

Figure 2b. The lattice fringes in the nanorods are clearly observed, which confirms that nanorods are structurally uniform. The interplanar spacing is 0.35 nm, combined with the results of FFT analysis (inset of Figure 2b); it is found to agree with the d spacing of (110) plane of VO_2(B).

In our experiment, the synthesis of VO_2(B) nanorods is carried out in the presence of CTAB without any reducing agent. CTAB is generally known as a efficient template in the preparation of 1-D nanostructures.[8] Very recently, Wang et al. reported that CTAB could act as reductant.[9] Though the exact growth mechanism is still under investigation, our experimental results indicated that CTAB may act not only as a template but also offer reducing atmosphere during the hydrothermal procedure. More research to demonstrate the exact formation mechanism is underway.

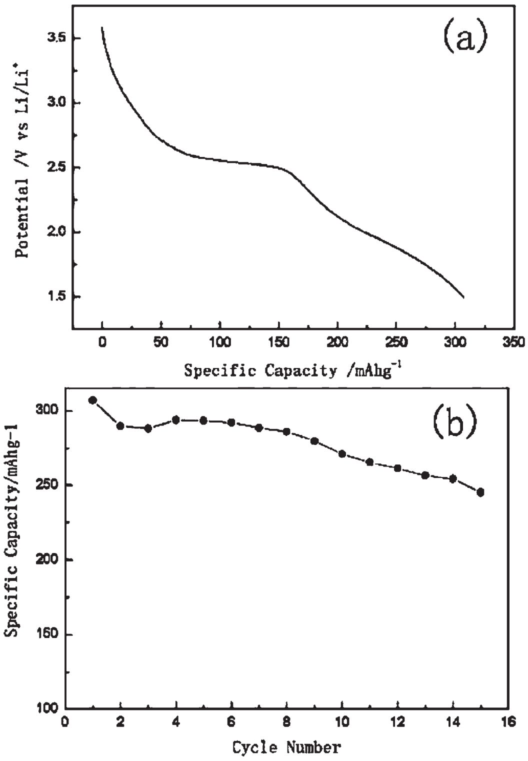

Figure 3. (a) Discharge curve of VO_2(B) nanorods during the first cycle recorded with a current density of 0.4 mA/cm^2. (b) Cycle performance of VO_2(B) nanorods in the range of 3.6–1.5 V.

The discharge curve of the cell with the as-synthesized VO_2(B) is illustrated in Figure 3a. VO_2(B) nanorods show a total reversible capacity of about 306 mAh/g in the potential range from 3.6 to 1.5 V, corresponding to an insertion of 1 Li into Li_xVO_2 and a reduction of some V^{4+} to V^{3+}. ($xLi^+ + xe^- + VO_2 \rightarrow Li_xVO_2$). The capacity is much higher than that of bulk VO_2(B) reported by Christian et al. (160 mAh/g).[2] The capacity at the end of 2.6–2.5 V voltage plateau is 151 mAh/g. Voltage begins to drop rapidly after the potential plateau, which means a polazation process results from the retardation of electrode reaction. Figure 3b illustrates the cyclability behavior of VO_2(B) nanorods .The specific capacity is 245 mAh/g after 15 cycles. VO_2(B) was found to have about 35% capacity decline after 15 cycles. In our experiments, VO_2(B) nanorods can maintain 80% of its initial capacity; this indicates the cylability behavior of that the VO_2 nanorods synthesized by this hydrothermal method have potentiality to be used as cathode material in rechargeable lithium batteries.

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References

1 K. Wilhelmi, K. Waltersson, and L. Kihlborg, *Acta Chem. Scand.*, **25**, 2657 (1971); K. Kawashima, K. Kosuge, and S. Kachi, *Chem. Lett.*, **1975**, 1131; F. Theobald, R. Cabala, and J. Bernard, *J. Solid State Chem.*, **17**, 431 (1976); G. Grymonprez, L. Fiermans, and J. Vennik, *Acta Crystallogr.*, **33A**, 834 (1977).

2 P. A. Christian, F. J. Di Salvo, and D. W. Murphy, U. S. Patent 4228226 (1980); M. J. Zhang and J. R. Dahn, *J. Electrochem. Soc.*, **143**, 2730 (1996); C. Tsang and A. Manthiram, *J. Electrochem. Soc.*, **144**, 520 (1997).

3 S. Iijima, *Nature*, **354**, 56 (1991); G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2446 (2002); Y. Dai, Y. Zhang, Y. Q. Bai, and Z. L. Wang, *Chem. Phys. Lett.*, **375**, 96 (2003); X. F. Duan, C. M. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman, *Nature*, **425**, 274 (2003).

4 F. Krumeich, H. J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, and R. Nesper, *J. Am. Chem. Soc.*, **121**, 8324 (1999); L. Q. Mai, W. Chen, Q. Xu, Q. Y. Zhu, C. H. Han, and J. F. Peng, *Solid State Commun.*, **126**, 541 (2003).

5 N. Pinna, M. Willinger, K. Weiss, J. Urban, and R. Shlögl, *Nano Lett.*, **3**, 1131 (2003).

6 Z. Gui, R. Fan, W. Q. Mo, X. H. Chen, L. Yang, S. Y. Zhang, Y. Hu, Z. Z. Wang, and W. Fan, *Chem. Mater.*, **14**, 5053 (2002).

7 J. C. Valmalette and J. R. Gavarri, *Mater. Sci. Eng., B*, **54**, 168 (1998).

8 X. Gao, C. M. Bender, and C. J. Murphy, *Langmuir*, **19**, 9065 (2003); M. H. Cao, C. W. Hu, G. Peng, Y. J. Qi, and E. B. Wang, *J. Am. Chem. Soc.*, **125**, 4982 (2003).

9 X. Wang and Y. D. Li, *Mater. Chem. Phys.*, **82**, 419 (2003).

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