Hydrothermal Synthesis of Metastable VO$_2$ Nanorods as Cathode Materials for Lithium Ion Batteries

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Metastable VO$_2$ nanorods, designated as VO$_2$(B) with diameters of 80–250 nm were synthesized via a PEG-assisted hydrothermal approach. The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) methods. The electrochemical properties of as-obtained VO$_2$(B) nanorods were studied by galvanostatic tests. The as-synthesized VO$_2$(B) nanorods showed an initial discharge capacity of 310 and 250 mA h g^{-1} in the 30th cycle in the potential range 1–3.5 V.

In recent years, vanadium oxides and their derivate compounds have attracted much attention because of their special physical and chemical properties, and potential applications in areas such as catalysis,[1] high-energy density lithium ion battery systems,[2] chemistry sensors,[3] electrochemical and optical device.[4] Vanadium usually forms a variety of binary oxides with the general formula VO$_{2+x}$ ($0 \leq x \leq 0.5$), such as V$_2$O$_5$, V$_6$O$_{13}$, V$_4$O$_9$, V$_3$O$_7$, and VO$_2$. The structure of these phases are built up of distorted VO$_6$ octahedra, which share both corners and edges.[5] Of these vanadium oxides, VO$_2$(B), one of metastable phases of vanadium dioxides, is of great interest owing to its layered structure and promising properties in electrochemistry field. VO$_2$(B) exhibits a maximum reversible capacity of about 320 mA h g^{-1} in lithium cells, which is more than twice the theoretical capacity of presently used cathode materials LiCoO$_2$ (140 mA h g^{-1}),[6] indicating it a promising alternative as cathode material in lithium ion battery considering its electrochemical, economical, and environmental merits.

It is well known that nanoscale materials often exhibit physical and chemical properties that differ greatly from their bulk counterparts. In the research field of battery system, Huynh et al. have reported that the operating properties of batteries depend not only on their structures but also on the morphology of the electrode components.[7] Tarascon and Armand have provided convincible experimental evidence that nanodimensional materials for lithium ion batteries possess improved electrochemical properties as compared to their bulk counterparts.[8] Further research shows that one-dimensional (1D) nanostructures are more prone to charge transport than the bulk crystalline structures, which may lead to greatly improved electrochemical properties. Traditionally, VO$_2$(B) was prepared by methods such as thermal reduction of V$_2$O$_5$ by H$_2$ or SO$_2$ gas, thermal decomposition of ammonium hexavanadate, and reduction of aqueous vanadate solution with potassium borohydride,[5,9] which only lead to bulk VO$_2$(B). Recently, there have been some reports about the synthesis of 1D nanostructures of VO$_2$(B), such as nanowires, nanorods, and nanobelts. However, all these synthesis methods are based on the reduction process of V^{5+} to V^{4+} using V$_2$O$_5$, NH$_4$VO$_3$, or expensive vanadium alkoxides as reagents.[10–13] To the best of our knowledge, the direct synthesis of VO$_2$(B) 1D nanostructures from reagents with the oxidation state of vanadi-

um at +4 is rarely reported before. Herein, we present a surfactant-assisted approach to metastable VO$_2$(B) nanorods using VOSO$_4$·xH$_2$O as reagents under hydrothermal conditions, and the electrochemical properties of as-synthesized VO$_2$(B) nanorods were studied by galvanostatic tests.

All the reagents used in the experiments were of analytical grade and were used without further purification. In a typical synthesis procedure, 0.2 g of VOSO$_4$·xH$_2$O was dissolved in 40 mL of distilled water, then 1 g of PEG-10000 was added in under magnetical stirring. The homogenous solution was transferred into a 50-mL Teflon-lined autoclave. Afterwards the autoclave was sealed and maintained at 180 °C for 24 h. After cooling to room temperature an standing, the black solid precipitate was collected and washed with distilled water and anhydrous alcohol for several times. The final product was dried in vacuum at 80 °C for 10 h.

The overall crystallinity and purity of as-synthesized samples were examined by XRD using a Philiphs X' Pert Super diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology and size distribution of the samples was examined by FESEM using a JEOL JSM-67700F SEM. The TEM images were obtained with a Hitachi 800 TEM with the accelerating voltage of 200 kV. Teflon cells were made to study the electrochemical properties of the product. The positive electrode consisted of the prepared VO$_2$(B) (80 wt %), carbon black (10 wt %), and polyvinylidene fluoride (PVDF, 10 wt %). The cells were assembled in an argon-filled glove box in which both the moisture and the oxygen levels were less than 1 ppm. The electrochemical tests were made in the voltage range of 1–3.5 V at a current density of 0.1 mA cm^{-2}.

The XRD pattern of the products is shown in Figure 1a, all the diffraction peaks can be indexed as metastable VO$_2$(B) phase (JCPDS Card No. 31-1438). The particle size of as-prepared VO$_2$(B) was estimated to be around 90 nm by Debye–Scherre formula. It can be observed from the XRD pattern that the 001, 002, 003 peaks are extraordinarily strong compared with other peaks, which differs greatly from the XRD data of the standard powder sample (JCPDS Card No. 31-1438), indicating that as-obtained
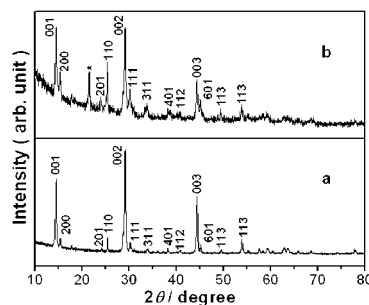

Figure 1. XRD patterns of the product (a) and the product after 50 cycles (b).
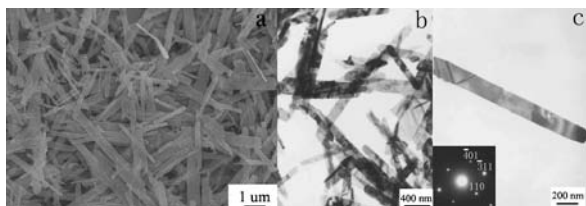
Figure 2. FESEM and TEM images of as-synthesized VO$_2$(B) nanorods (Inset in Figure 2c: SAED pattern of an individual VO$_2$(B) nanorod).

VO$_2$(B) may have special morphologies. No impurity phases are detected from the XRD pattern such as V$_2$O$_5$, VO$_2$(R), and VO$_2$(M), indicating that VO$_2$(B) nanorods with high purity were obtained under current synthetic conditions.

The morphology of the samples was observed by FESEM test, which were shown in Figure 2a. Large amounts of VO$_2$(B) nanorods were obtained by our synthetic route. The diameter of the nanorods ranges from 80 to 250 nm, and the length is up to several micrometers. Further structural information of the products is provided by TEM tests, which were shown in Figures 2b and 2c. Figure 2b showed the TEM image of tens of VO$_2$(B) nanorods with the diameter range between 100–250 nm, which agreed well with the result of the XRD and SEM test. A single nanorod of VO$_2$(B) sample is shown in Figure 2c, which has the diameter around 100 nm. The SAED pattern taken on the single nanorod is given in the inset of Figure 2c, indicating that the nanorods were well single crystallined, and the growth direction was along c axis.

The addition of PEG may be the decisive factor in the synthesis of VO$_2$(B) nanorods. Firstly, according to Pearson's results,[14] the –O– of the ether group on the PEG chains has a strong basic property and possesses a pair of electrons, which facilitates the formation of VO$_2$(B) products in the hydrothermal conditions, thus the reaction temperature is lowered. Secondly, PEG is a non-ionic polymer whose chain contains many hydrophilic (–O–) and hydrophobic (–CH$_2$–CH$_2$–) sites. And the chain has a high degree of flexibility so that the C–O bond is very easy to rotate. The high flexibility of the chain and its ability to be a donor of oxygen atoms enables it to couple with VO^{2+} ions and to form thermodynamically favorable polymer complex, which induces the successful growth of VO$_2$(B) nanorods under hydrothermal conditions. Comparative experiment was made without the participation of PEG while keeping other parameters unchanged, and no products were obtained, indicating that the addition of PEG-10000 is indispensable in our synthetic route.

The electrochemical property of the products is studied by galvanostatic test. Figure 3a shows the first charge/discharge curve of the VO$_2$(B) nanorods at room temperature. The initial discharge capacity of the products reaches 310 mA h g^{-1}, which has nearly reached the theoretical capacity of VO$_2$(B) and is far more better than currently used LiCoO$_2$ and LiMn$_2$O$_4$ cathode materials. Thirty cycles were tested to study the cycleability of the VO$_2$(B) nanorods. Figure 3b gives the cycling behavior of the VO$_2$(B)/Li cells. About 80% of initial discharge capacity is reserved after 30 charge/discharge cycles, indicating that as-synthesized VO$_2$(B) nanorods have rather satisfying cycleabilities for applications in lithium ion batteries. XRD test was applied on the sample after 30 charge/discharge cycles, and the result is shown in Figure 1b. The cycled sample remains mainly the VO$_2$(B) structure, though the baseline is not as smooth as the sample before the galvanostatic test, indicating the good structure
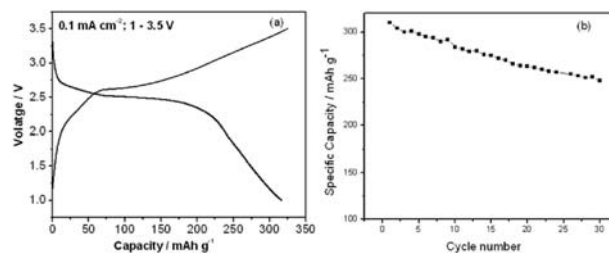

Figure 3. (a) First charge/discharge curve of as-synthesized VO$_2$(B) nanorods; (b) Cycle performance of VO$_2$(B) nanorods in the voltage range of 3.5–1 V.

stability of as-synthesized VO$_2$(B) nanorods during the charge/discharge cycles. Several possible explanations can be provided for the improved electrochemical performances of as-synthesized VO$_2$(B) nanorods. One is that the insertion of Li ions into the cathode materials is diffusion limited, which is a kinetic factor. The diffusion length of Li ions in the VO$_2$(B) nanorods is much shorter than that of bulk materials, which is beneficial for the electrode kinetics and favors the charge-transport process in the charge/discharge cycles,[15,16] thus the electrochemical properties of the samples can be greatly improved. Another explanation is that the VO$_2$(B) nanorods have high surface areas, thus the number of electrochemical active positions is greatly increased, which leads to the improvement of electrochemical properties.[17,18] The one-dimensional (1-D) nanostructured electrode materials are the smallest dimensional structures for efficient electron transport and can be used to detect the theoretical operation limits of lithium ion batteries,[19] thus leading to their superior electrochemical performances compared with other morphological nanostructured electrode materials.

In summary, metastable VO$_2$(B) nanorods were synthesized via a PEG-assisted hydrothermal route. The products were characterized by XRD, SEM, and TEM methods. The electrochemical performances of as-synthesized VO$_2$(B) nanorods were studied by galvanostatic tests, indicating them as promising cathode materials for application in the lithium ion battery industries.

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