Research Article

Fabrication of VO₂ (B) Nanobelts and Their Application in Lithium Ion Batteries

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VO₂ (B) nanobelts have been successfully synthesized via a simple hydrothermal route. The products were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and Raman spectrum. These nanobelts are of rectangular cross-section with mean length about 1 μ m, mean width about 80 nm, and mean thickness about 50 nm. The as-synthesized VO₂ nanobelts were assembled as the cathode electrodes of lithium ion batteries. Their electrochemical properties were studied by conventional charge/discharge tests, which show an initial discharge capacity of 321 mAh g⁻¹ with voltage plateau near 2.5 V. These results indicated that such hydrothermally synthesized VO₂ (B) nanobelts could be an ideal candidate of cathode material for lithium ion battery.

1. Introductions

During the past few years, vanadium-oxides-based materials have attracted much attention due to their fascinating structures and electronic, optical, and magnetic properties, which are relevant to such diverse areas as lubrication, chemical sensor, catalysis, cathode materials in batteries, and minerals [1–7].

Metastable phase oxide VO₂ (B) is built up of distorted VO₆ octahedra sharing edges and corners [8] and has been found to be of interesting cathode properties in lithium ion batteries [9]. However, VO₂ (B) is very difficult to synthesize by conventional high temperature procedures because the phase change from metastable VO₂ (B) to thermodynamically more stable rutile VO₂ will occur at $T > 300^{\circ}\text{C}$ and the latter shows no attractive electrochemical properties [10]. The synthesis of VO₂ (B) hierarchical structures is generally achieved via low-temperature chemical methods [8, 11–13], which can hardly be separated from toxic reducing agent and usually need long reaction time. So we are interested in developing simple methods to synthesize VO₂ (B) nanostructures using nontoxic reducing agent and exploring its morphology-related electrochemical properties. Among

different nanostructures, one-dimensional (1D) nanostructured VO₂ (B) has attracted special attention due to its high surface-to-volume ratio, which is strongly relevant to its electrochemical performances. VO₂ (B) nanowires, nanobelts, nanoribbons, nanoneedles, and nanorods were respectively synthesized [14–18]. To the best of our knowledge, the synthesis of 1D nanostructured VO₂ (B) with rectangular cross-section is rarely achieved due to the intrinsic growth habit of VO₂ (B) crystal [13]. Here, we report a simple hydrothermal approach to synthesize VO₂ (B) nanobelts with rectangular cross-section using nontoxic glucose as reducing agent, and its electrochemical properties are studied by conventional charge/discharge tests.

2. Experimental

All the chemicals were of analytical grade and purchased from Shanghai Chemical Reagents. In a typical procedure, 1 mmol V₂O₅ and 0.5 mmol glucose were dissolved in 30 mL distilled water, and then 0.5 g sodium sulfate was put into the solution. After stirring for 20 minutes, the obtained homogeneous yellowy suspension was transferred into a 50 mL teflon-lined autoclave, and distilled water was

FIGURE 1: XRD pattern of the as-synthesized products.

subsequently added up to 80% of its capacity. The autoclave was at last sealed and placed in an oven, heated at 160°C for 24 h. The precipitate was centrifuged with distilled water and ethanol both for 4 times and dried in an oven at 60°C for 24 h.

The morphology and structure of the resulting products were characterized by field-emission scanning electron microscopy (FE-SEM S-4800, Hitachi), X-ray powder diffraction (Rigaku RINT2400 with Cu K α radiation), and micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV, YGA 532 nm). For fabricating of lithium ion batteries, a mixture of 80 wt% of active material, 10 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP) solution (0.02 g mL⁻¹) was coated on aluminum foil and cut into disc electrodes with a diameter of 14 mm using a punch. Coin-type cells (2025) of Li/1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v + VC)/VO₂ were assembled in an argon-filled glove box. A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage region between 1.5 V and 3.75 V with a multichannel batteries test system (LAND CT2001A).

3. Results and Discussion

Typical XRD pattern of the as-synthesized products is shown in Figure 1. All diffraction peaks can be indexed as monoclinic cell of VO₂ (B) with cell parameters $a = 12.03$ Å, $b = 3.693$ Å, and $c = 6.42$ Å, which is in good agreement with the JCPDS, no. 31-1438, indicating the formation of pure phase VO₂ (B). The strong and sharp diffraction peaks suggest that the as-synthesized products are well crystallized.

Figure 2(a) is a low magnification SEM image of the as-synthesized VO₂ (B), showing a large quantity of nanobelts. For further clarification of the morphology and size of those nanobelts, an SEM image with high magnification is shown in Figure 2(b). It can be found that those nanobelts are of rectangular cross-section with mean length about 1 μ m,

(a)

(b)

FIGURE 2: SEM images of the products with low (a) and high (b) magnification.

FIGURE 3: Raman spectrum of the products.

mean width about 80 nm, and mean thickness about 50 nm, respectively.

As shown in Figure 3, Raman spectrum in the wavelength range of 150 cm⁻¹ ~ 1500 cm⁻¹ is dominated by the peaks at 170 cm⁻¹, 271 cm⁻¹, 438 cm⁻¹, 519 cm⁻¹, 705 cm⁻¹, and 985 cm⁻¹, and these peaks are the vibration bands of VO₂

FIGURE 4: Initial two discharge and charge curves of the electrode made of VO_2 (B) nanobelts.

(B) [12]. The peaks at 170 cm^{-1} and 271 cm^{-1} can be assigned to V–O–V bending modes and external mode (bending/wagging), respectively. The peaks at 438 cm^{-1} and 519 cm^{-1} are attributed to V–O–V stretching mode. The peak at 705 cm^{-1} is due to coordination of vanadium atoms with three oxygen atoms, while the peak at 985 cm^{-1} is attributed to V=O stretching of distorted octahedral and distorted square-pyramids [19–22]. These Raman results are highly accordant with above XRD pattern and further confirm the formation of monoclinic VO_2 (B).

Figure 4 is the 1st and 2nd discharge and charge curves of VO_2 (B) nanobelts electrode at a current density of 214 mA g^{-1} . It shows a high initial discharge capacity of 316 mAh g^{-1} with clear voltage plateau near 2.5 V , while the first charge capacity is 321 mAh g^{-1} with distinct voltage plateau near 2.62 V . The charge and discharge capacities show little attenuation, which indicates a highly reversible intercalation and extraction of Lithium ions. In the 2nd discharge and charge curve, the discharge and charge capacities are 323 mAh g^{-1} and 319 mAh g^{-1} and the voltage plateaus locate at near 2.52 V and 2.64 V , respectively. The charge and discharge behavior of our VO_2 (B) nanobelts is similar to that reported in the literature [13, 17, 18], but with smaller capacity attenuation. We propose that the unique synthesis environment in hydrothermal method and the special morphology of the as-synthesized VO_2 (B) nanobelts are the causations of its good electrochemical performance.

4. Conclusion

In conclusion, VO_2 (B) nanobelts with rectangular cross-section are synthesized via a simple hydrothermal route. Electrochemical properties of the as-synthesized VO_2 nanobelts as cathode electrode of lithium ion batteries are studied by conventional charge/discharge tests, which show high discharge/charge capacity and steady voltage plateaus, indicating that it is suitable for the application in lithium ion batteries as cathode electrode material.

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