Solvothermal Synthesis of γ-LiV$_2$O$_5$ Nanorods as Cathode Material for Rechargeable Lithium Batteries

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γ-LiV$_2$O$_5$ nanorods with diameters of 30–40 nm and lengths of 0.4–2 μm have been synthesized by a simple solvothermal method at 160 °C using ethanol as a solvent, which also serves as a reducing agent. The γ-LiV$_2$O$_5$/Li cell demonstrated an initial specific capacity of 259 mAh/g. After several initial cycling, the cell showed stabilized cycling behavior (199 mAh/g at the 20th cycle).

γ-LiV$_2$O$_5$ has been extensively investigated as a class of low-cost cathode material in rechargeable lithium batteries.[1–3] However, it is difficult to synthesize γ-LiV$_2$O$_5$ because there are two valence states (V^{5+} and V^{4+}) of vanadium co-existing in this compound. By conventional solid-state reaction[2] or wet-chemistry method,[3] the mixture of LiVO$_3$, V$_2$O$_5$, and VO$_2$ or V$_2$O$_3$ was heated at 350–600 °C under vacuum or N$_2$ protected atmosphere in order to control the valence balance of V^{4+} and V^{5+}. Another synthetic method is a procedure described by Murphy et al.,[4] in which V$_2$O$_5$ was reduced with appropriate amount of lithium iodide in acetonitrile under argon. The above methods are complicated and cost a deal. Moreover, such routes are faced with difficulty to control the homogeneity and particle size of the final products. It is known that the electrochemical behavior of cathode materials strongly depends on the particle size: the smaller the particle size, the lower the cell polarization and the higher the cell capacity.[5] In our study, a simple and mild solvothermal method was employed to synthesize γ-LiV$_2$O$_5$ by using ethanol as a solvent as well as a reducing agent.

Twenty millimole of each analytically pure LiOH and V$_2$O$_5$ were put into a Teflon-lined stainless steel autoclave of 50 mL capacity. The autoclave was filled with ethanol up to 80% of the total volume. After the autoclave was kept at 160 °C under autogeneous pressure for 24 h, it was allowed to cool to room temperature naturally. The as-formed solid precipitate was filtered, washed with ethanol, and dried at 100 °C for 2 h.

Electrochemical tests were performed in cells 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 active material, acetylene black and poly (tetrafluoroethylene) (PTFE) (80:10:10). 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 0.3 mA/cm^2, in a range of 1.5–4.2 V. All tests were performed at room temperature.

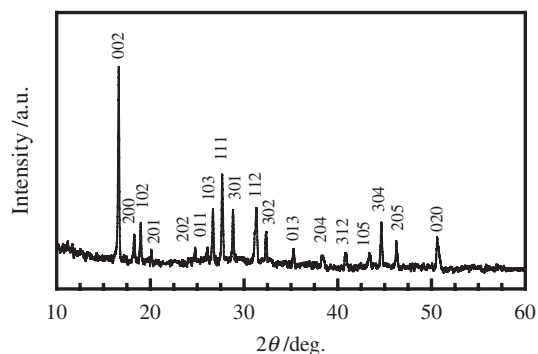The X-ray diffraction (XRD) pattern of the as-synthesized

Figure 1. XRD pattern of γ-LiV$_2$O$_5$ nanorods.

black product is shown in Figure 1. All the diffraction peaks are identical to those of orthorhombic γ-LiV$_2$O$_5$ according to JCPDS card 18-756. No impurity phases such as V$_2$O$_5$, Li$_3$VO$_4$ and LiVO$_2$ are detected in the product from its XRD pattern. The yield of this synthetic route is about 94%.

In our experiment, the synthesis of γ-LiV$_2$O$_5$ is carried out using a great excess of ethanol as a solvent through a solvothermal process. To the ethanol, a portion of it is oxidized (by V$_2$O$_5$) to aldehyde, which is experimentally confirmed through chemical analysis of the final solution mixture. From the above results, it can be seen that the ethanol acts not only as a solvent but also as a reducing agent in the synthesis of γ-LiV$_2$O$_5$ powders. Thus, the formation mechanism of γ-LiV$_2$O$_5$ through the reaction of LiOH, V$_2$O$_5$ and excess ethanol under the solvothermal condition can be expressed as follows:
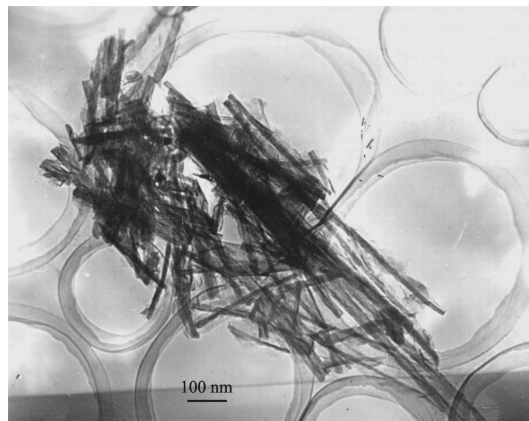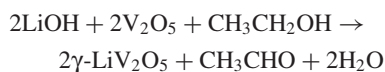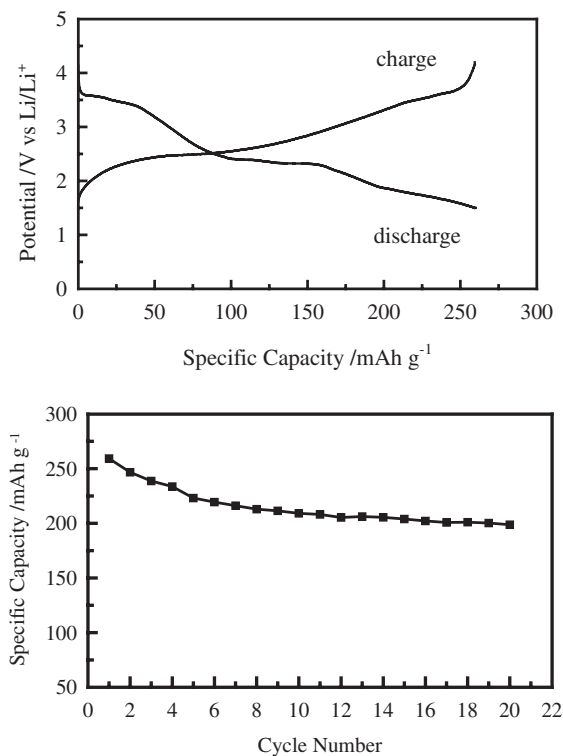

Figure 2. TEM image of γ-LiV$_2$O$_5$ nanorods.

$$2LiOH + 2V_2O_5 + CH_3CH_2OH \rightarrow$$
$$2\gamma\text{-}LiV_2O_5 + CH_3CHO + 2H_2O$$

A typical transmission electron microscopy (TEM) image

Figure 3. (a) Charge-discharge curves of the cell with γ-LiV$_2$O$_5$ nanorods during the first cycle. Current density: $0.3\,mA\cdot cm^{-2}$. (b) Cycle performance of the cell with γ-LiV$_2$O$_5$ nanorods.

of the as-synthesized γ-LiV$_2$O$_5$ is shown in Figure 2. It clearly shows that γ-LiV$_2$O$_5$ particles have a rod-like morphology with diameters of 30–40 nm and lengths of 0.4–2 μm.

The charge-discharge curves of the cell with the as-synthesized γ-LiV$_2$O$_5$ during the first cycle are illustrated in Figure 3(a). It can be seen that the specific discharge capacity of the cell attains 259 mAh/g in the range of 1.5–4.2 V. The capacity at the end of 2.4–2.3 V voltage plateau is 157 mAh/g. Figure 3(b) shows the cycle performance of the cell. In the first 5 cycles, the specific capacity reduces quickly and then maintains stable in the subsequent cycles. The specific capacity is 199 mAh/g after 20 cycles. It indicates that the γ-LiV$_2$O$_5$ nanorods synthesized by this solvothermal method have potentiality to be used as a cathode material in rechargeable lithium batteries.

In summary, a simple and low-cost solvothermal method has been developed to synthesize γ-LiV$_2$O$_5$ nanorods by using ethanol as a solvent as well as a reducing agent. Preliminary electrochemical tests indicated that the γ-LiV$_2$O$_5$/Li cell has an initial specific capacity of 259 mAh/g in the range of 1.5–4.2 V. Further work is under the way to improve the electrochemical performance of these γ-LiV$_2$O$_5$ nanorods.

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