Hydrothermal Synthesis of MnV$_2$O$_6$ Nanorods as an Anode Material for Lithium-ion Batteries

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Abstract. The MnV$_2$O$_6$ nanorods anode materials was prepared by a simple hydrothermal method, MnCl$_2$·2H$_2$O and NH$_4$VO$_3$ as raw stuffs. The MnV$_2$O$_6$ nanorods anode materials were tested by SEM, XRD, and galvanostatic charge/discharge profile measurement. Time-dependent experiments were designed to examine the morphology evolution of the MnV$_2$O$_6$ nanorods anode materials. As an anode material, the MnV$_2$O$_6$ nanorods showed the good discharge capacity (403 mAh g$^{-1}$ of 100th). The good electrochemical performance can be attributed to the synergistic effect with Mn and V elements, and fast lithium ion diffusion of the 1D nanorods structure.

1 Introduction

Lithium ion battery (LIBs) have been more and more widely used with pure electric vehicles, hybrid electric vehicles, mobile electronic products, et.al [1]. However, commercialization anode material (graphite: 372 mAh g$^{-1}$) limit the further development and application of LIBs. So the development of low cost, non-toxic, long cycle life of electrode materials become the urgent demand of the LIBs [2]. In all TMOs (transition metal oxides), metal vanadates have been used in catalytic, optical, and electrode materials fields [3]. According to the literature, metal vanadates (such as Co$_3$V$_2$O$_8$, CoV$_2$O$_6$, FeVO$_4$, MoV$_2$O$_8$, Ni$_3$V$_2$O$_8$, and Cu$_3$V$_2$O$_8$) also have good electrochemical performance, which can be used well in electrode materials (lithium-ion batteries, sodium-ion battery, zinc ion battery, et al.) [4–6].

MnV$_2$O$_6$ have generated remarkable attention because of the facile preparation, safety, and high theoretical capacity. Some reports were related to research it as anode materials, the electrochemical property of pure MnV$_2$O$_6$ is dissatisfactory, they have modified the MnV$_2$O$_6$ by means of coating, compounding and constructing nanostructures to achieve the purpose of improving electrochemical performance. Kim and Ikuta synthesized a brannerite structure MnV$_2$O$_6$ by a polymer gelation method, and the MnV$_2$O$_6$ electrode material displayed a high initial discharge capacity [7]. In this work, the MnV$_2$O$_6$ nanorods anode materials was prepared by a simple hydrothermal method. The morphology, crystal structure and electrochemical properties of the prepared composites were systematically investigated.

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Time-dependent experiments were designed to examine the morphology evolution of the MnV$_2$O$_6$ nanorods anode materials.

## 2 Experimental

Firstly, MnCl$_2$·2H$_2$O and NH$_4$VO$_3$ with stoichiometric amounts ratio of 1:2 were dissolved in 30 ml distilled water under magnetic stirring for 1 h. Then the mixed solution was transferred into a 50 mL teflon-lined stainless steel autoclave and annealed at 180 °C for 24 h. After naturally cooled down to room temperature, the resulting product was collected by filtration, and washed with deionized water and absolute alcohol for three times. It was further dried at 60 °C for 12 h.

The crystal structure and surface morphologies of the MnV$_2$O$_6$ were characterized by X-ray diffraction (XRD) with Cu Kα radiation (Bruker AXS, D8 diffractometer) and scanning electron microscopy (SEM; JEOL JSM, 6510 V). The typical Electrochemical measurements process of MnV$_2$O$_6$ material could be briefly shown in ref [8].

## 3 Results and discussion

The morphologies of the as-obtained MnV$_2$O$_6$ sample was measured via SEM. The morphology of the MnV$_2$O$_6$ sample was shown in Fig. 1a and b, which emerges severe aggregation of irregular nanorods structure, and the nanorods morphology of MnV$_2$O$_6$ sample is composed of non-uniform nanorods (diameters of ~ 200 nm and length of 2~10 μm). Fig.1c showed the XRD patterns of the MnV$_2$O$_6$ nanorods sample. The diffraction peaks can be indexed to the cubic phase of MnV$_2$O$_6$ (JCPDS No.35-0139). The identified diffraction peaks at 14.2, 20.0, 20.6, 27.2, 28.2, 29.3, 36.8, 38.6, 40.5, 40.7, 41.8, 43.5, 47.3, 47.8, 48.3, 51.7, 54.3, and 55.7° can be well assigned to (001), (20-1), (200), (110), (20-2), (201), (-112), (-311), (310), (111), (202), (003), (311), (-403), (-113), (020), (-204), and (-113) planes of MnV$_2$O$_6$. The MnV$_2$O$_6$ sample exhibit sharp diffraction peaks, indicating the well crystallization.

Fig. 1. SEM images (a and b) and XRD pattern (c) of the MnV$_2$O$_6$.

To confirm the formation mechanism of the MnV$_2$O$_6$ nanorods, time-dependent experiments were designed to examine the morphology evolution of the sample under different reaction times in Fig. 2. The morphologies of the as-obtained five compounds were measured via SEM. The morphology of the MnV$_2$O$_6$ (1 h) was shown in Fig. 2a, which emerges severe aggregation of irregular particles. After reaction time of 3 h, the morphology changed significantly, the morphology was made up nanoparticles and nanorods. As the reaction time continued to increase, the morphology continued to change. After reaction time of 12 h, the morphology was consisted of a small number of
Time-dependent experiments were designed to examine the morphology evolution of the MnV2O6 nanorods anode materials.

2 Experimental

Firstly, MnCl2·2H2O and NH4VO3 with stoichiometric amounts ratio of 1:2 were dissolved in 30 ml distilled water under magnetic stirring for 1 h. Then the mixed solution was transferred into a 50 mL teflon-lined stainless steel autoclave and annealed at 180 °C for 24 h. After naturally cooled down to room temperature, the resulting product was collected by filtration, and washed with deionized water and absolute alcohol for three times. It was further dried at 60 °C for 12 h.

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Fig. 2. SEM images (a and b) and XRD pattern (c) of the MnV2O6.

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Fig. 2. SEM images of the precursors obtained after different reaction times: (a) 1 h, (b) 6 h, (c) 6 h, and (d) 12 h. (e) Schematic illustration of the formation process for the MnV2O6 nanorods.

Fig. 3a shows the discharge-charge curves of the MnV2O6 electrode at a constant current density of 200 mA g⁻¹. The beginning discharge specific capacity of the MnV2O6 electrode is 1123 mAh g⁻¹, which can be attributed to store 10.2 Li mole of MnV2O6. The extra specific capacity can be attributed to the SEI (solid electrolyte interphase) layer, which be formed by the decomposition of solvent in the electrolyte solution [10]. It can be seen that the MnV2O6 electrode is 709.6 mAh g⁻¹ of the 2nd cycle, which means 36.8% of the first capacity loss. The samples respectively retain capacity of 403 mAh g⁻¹ of 100th cycle. Huang and Gao synthesized uniform MnV2O6 nanobelts as anode materials by a hydrothermal method; the MnV2O6 nanobelts displayed high cycling stability (1085 mAh g⁻¹ at 100 mA g⁻¹) and rate capability [11]. Some research work to improve rate performances by coating or composite method for its application in our working. For example, polymer coating of MnV2O6 materials and MnV2O6/graphene nanocomposites are also well known to be for improving electrode performance because it is simple, low cost, and scalable. The MnV2O6 nanorods electrode exhibits higher capacity. Outstanding electrochemical properties for the MnV2O6 nanorods attributed to one dimensional nanorod structure can provided a larger surface area, shorter lithium ion diffusion path, maintain stable structure, guaranteed the good rate performance[4]. Fig. 3c shows the CV curves of MnV2O6 electrode at 0.1 mV s⁻¹. During the first cathodic scans, the peaks of MnV2O6 electrode at 1.89, 1.30, 0.63, 0.41 and 0.05 V were corresponding to the reduction of MnO and V2O5 to form MnO⁺ and Liₓ+yV2O5 as well as formation of SEI. In the following scan, the reduction peaks moved to 0.74 V and 0.50 V. The anodic scans feature three oxidation peak at 0.19, 0.65, 0.85 and 2.52V, which could be associated with the oxidations of Mn to MnO, Liₓ+yV2O5 to LiₓV2O5 and the decomposition of Li₂O. Furthermore, the CVs of MnV2O6 electrode remain almost the same of the follow cycle, which can also indicate that the good
rate performance of MnV₂O₆ electrode. The possible electrochemical reactions of the MnV₂O₆ electrode was as follows [7,11]:

\[
\begin{align*}
\text{MnV}_2\text{O}_6 + x \text{Li}^+ + xe^- &\rightarrow \text{MnO} + \text{Li}_x\text{V}_2\text{O}_5 \quad (1) \\
\text{MnO} + 2\text{Li}^+ + 2e^- &\rightarrow \text{Mn} + \text{Li}_2\text{O} \quad (2) \\
\text{LixV}_2\text{O}_5 + y\text{Li}^+ + ye^- &\rightarrow \text{Li}_x+y\text{V}_2\text{O}_5 \quad (3)
\end{align*}
\]

Fig. 3. (a) Discharge-charge curves of the MnV₂O₆ sample for the 1ˢᵗ, 2ⁿᵈ, 2₀ᵗʰ, 5₀ᵗʰ and 1₀₀ᵗʰ cycles at a constant current density of 2₀₀ mA g⁻¹, (c) Cycling performance of the MnV₂O₆ electrode, (c) cyclic voltammograms of the MnV₂O₆ electrode at the rate of 0.₁ mV s⁻¹.

4 Conclusions

In this work, the MnV₂O₆ nanorods anode materials was prepared by a simple hydrothermal method, MnCl₂·2H₂O and NH₄VO₃ as raw stuffs. The MnV₂O₆ nanorods anode materials were tested by SEM, XRD, and galvanostatic charge/discharge profile measurement. Time-dependent experiments were designed to examine the morphology evolution of the MnV₂O₆ nanorods anode materials. As an anode material, the MnV₂O₆ nanorods showed the good discharge capacity (4₀₃ mAh g⁻¹ of 1₀₀th). The good electrochemical performance can be attributed to the synergistic effect with Mn and V elements, and one dimensional nanorod structure can provided a larger surface area, shorter lithium ion diffusion path, and maintain stable structure.

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rate performance of MnV2O6 electrode. The possible electrochemical reactions of the MnV2O6 electrode was as follows [7,11]:

\[ \text{MnV}_2\text{O}_6 + x \text{Li}^+ + x\text{e}^- \rightarrow \text{MnO} + \text{Li}_x\text{V}_2\text{O}_5 \] (1)

\[ \text{MnO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Mn} + \text{Li}_2\text{O} \] (2)

\[ \text{Li}_x\text{V}_2\text{O}_5 + y\text{Li}^+ + y\text{e}^- \rightarrow \text{Li}_{x+y}\text{V}_2\text{O}_5 \] (3)

Fig. 3. (a) Discharge-charge curves of the MnV2O6 sample for the 1st, 2nd, 20th, 50th and 100th cycles at a constant current density of 200 mA g$^{-1}$, (c) Cycling performance of the MnV2O6 electrode, (c) cyclic voltammograms of the MnV2O6 electrode at the rate of 0.1 mV s$^{-1}$.

Conclusions

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