Facile synthesis of ammonium vanadium oxide nanorods for Na-ion battery cathodes

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A B S T R A C T

A simple and versatile method for preparation of $NH_4V_4O_{10}$ nanorods is developed via a simple hydrothermal route. $NH_4V_4O_{10}$ nanorods display better cycling stability than $NH_4V_4O_{10}$ microflowers as a cathode material for sodium-ion batteries because of the changes in crystalline structure, which would be in favor of superior discharge capacity. Furthermore, the enhancement of electrochemical performance for $NH_4V_4O_{10}$ nanorods at high current rates is offered in addition of fluoroethylene carbonate to electrolyte. Such a good performance results from the improvement of reaction kinetics and Na-ion transfer rate.

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1. Introduction

Nowadays, there is a remarkable demand for rechargeable batteries with reversible and efficient electrochemical energy storage and conversion in the field of portable electronic consumer devices, electric vehicles, and large-scale electricity storage in smart and intelligent grids [1]. Sodium-ion battery is one of the promising rechargeable batteries for its huge abundant and low cost sodium resources [2]. The current concerns are leading to an increasing interest in low cost, high safety electrode materials with long cycle life and favorable battery electrolyte in the sodium-ion battery. Now people in growing numbers are coming to report and investigate the electrochemical properties of various new electrode materials, such as a NASICON-Type structured $Na_3Ti_2PO_4$ [3], layered Na_2FePO_4F and olivine $Na(Fe, Mn)PO_4$ [4], $Na_4Mn_9O_{18}$ newswires [5], $Na_x[Fe_{1/2}Mn_{1/2}]O_2$ [6], rhombohedral $Na_{1.72}$ $MnFe(CN)_6$ and cubic $Na_{1.40}MnFe(CN)_6$ [7], amorphous phosphorus-carbon (a-P–C) composite [8], Cu_2Se [9] and so on.

Vanadium oxides and bronzes offer the advantages of being cheap, easy to synthesize, plenty of the earth and high-energy density. Therefore, they have attracted much interest in energy conversion and storage [10]. However, few investigations of vanadium oxides and bronzes were performed for sodium-ion battery electrode materials. Hamani et al. reported the electrochemical properties vs. Na of the layered Na_xVO_2 phases having either

octahedral or trigonal prismatic symmetries, which could reversibly insert 0.5 Na atoms per unit formula leading to sustain a reversible capacity of nearly 120 mA h g^{-1} [11]. NaV_6O_{15} nanorods also displayed stable sodium-ion insertion–deinsertion reversibility and delivered 142 mA h g^{-1} sodium ions when worked at a current density of 0.02 Ag^{-1} [12]. But the capacity and cycling stability of Na_xVO_2 and NaV_6O_{15} cathode materials should be improved dramatically. Recently, a nanoscale ordered bilayered V_2O_5 cathode material was operated at room temperature and it showed the theoretical capacity of 250 mA h g^{-1} for small diffusion length and large surface area [13]. Single-crystalline bilayered V_2O_5 nanobelts also exhibited a high capacity of 231.4 mA h g^{-1}. It corresponded to the theoretical capacity to form $Na_2V_2O_5$ on Na-ion insertion [14]. Hollow VOOH microspheres presented a high capacity of 150 mA h g^{-1} [15]. However, few people paid full attention to ammonium vanadium oxide cathode materials for lithium-ion and sodium-ion battery [16,17]. Amongst various ammonium vanadium oxides, $NH_4V_4O_{10}$ has not been proposed as a cathode material for rechargeable sodium-ion batteries. Recently, great interest has been attracted to develop various methods for the preparation of $NH_4V_4O_{10}$ nanobelts and microflowers with an application to lithium-ion battery [18,19] and photocatalysis [20].

Herein, we report the synthesis of $NH_4V_4O_{10}$ nanorods via a simple hydrothermal method requiring low cost manufacturing and ultra-low power consumption. $NH_4V_4O_{10}$ was prepared with controlled phase structure and morphology by the addition of magnesium nitrate. When $NH_4V_4O_{10}$ nanorods were used as cathode materials for sodium-ion batteries, they showed better cycling stability than $NH_4V_4O_{10}$ microflowers. In addition, an investigation

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of $NH_4V_4O_{10}$ nanorods electrochemical performance at high current rates was achieved after addition of fluoroethylene carbonate to electrolyte.

2. Materials and methods

$NH_4V_4O_{10}$ nanorods were prepared according to the following procedure. 0.16 g oxalic acid and a certain amount of magnesium nitrate was dissolved in 30 ml deionized water, and then 0.2 g ammonium metavanadate (NH_4VO_3) was added into the solution under stirring at room temperature for 2 h. After that, the mixture was transferred to a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 24 h and cooled to room temperature.

$NH_4V_4O_{10}$ microflowers were prepared under the similar condition. 1.28 g oxalic acid and 0.4 g NH_4NO_3 were dissolved in 30 ml deionized water, and then 0.59 g NH_4VO_3 was added into the solution under stirring at room temperature for 2 h. After that, the mixture was transferred into a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 24 h and cooled to room temperature.

The as-synthesized materials were observed by Hitachi S-4800 field emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, and X'Pert). A Land CT2001A battery tester was used to measure the electrode activities at room temperature. Cyclic voltammetry (CV) experiments were performed with a Chi660c electrochemical workstation at a scan rate of 1 mV s^{-1}.

The test of $NH_4V_4O_{10}$ microflowers and nanorods as cathode materials for sodium-ion batteries was performed. The composite positive electrode was consisted of the active material, a conductive material (super-pure carbon) and binder (PVDF) in a weight ratio of 7/2/1. The Na metal was used as the counter electrode. The electrolyte was 1 M $NaClO_4$ in the propylene carbonate (PC) solvent. The cells were charged and discharged between a 1.5–3.4 V voltage limit at different discharge rates. 1 M $NaClO_4$ in the PC solvent with addition of fluoroethylene carbonate (FEC) was also used as an electrolyte for $NH_4V_4O_{10}$ nanorods and vanadium precursor nano-platelets prepared without magnesium nitrate.

3. Results and discussion

The effects of magnesium nitrate on the finally formed crystalline structures of ammonium vanadium oxide were investigated by means of wide angle X-ray diffraction (WAXD). The results show that magnesium nitrate has a tremendous influence on the crystalline structure of precursors. XRD was used to identify the crystalline structure of precursors prepared in the absence of magnesium nitrate in Fig. 1a. The strong diffraction peak at 9.83° with a d-spacing of 8.99 Å is very close to the d-spacing (8.92 Å) of $(NH_4)_2V_4O_9$ (JCPDS 23-0791) in Fig. 1a. But other diffraction peaks cannot be ascribed to $(NH_4)_2V_4O_9$, VO_2, V_2O_5 and vanadium oxide hydrate. When 0.1 g magnesium nitrate was added, $NH_4V_4O_{10}$ was also obtained, as shown in Fig. 1b. A complicated phase was prepared with a further increasing of magnesium nitrate to 0.2 g. All its diffraction peaks cannot be ascribed to any known compounds listed in the XRD-databases in Fig. 1c. To draw a comparison, the other $NH_4V_4O_{10}$ was also prepared with NH_4VO_3, NH_4NO_3, oxalic acid and water, as shown in Fig. 1d. It can be found that there are some differences in diffraction peaks between the two $NH_4V_4O_{10}$ by careful observations. The $NH_4V_4O_{10}$ prepared with magnesium nitrate (111) diffraction peaks are stronger than that (110) diffraction peaks, while the $NH_4V_4O_{10}$ prepared with NH_4NO_3 (111) diffraction peaks are weaker than that (110) diffraction peaks. It implies that Mg^{2+} and NH_4^+ have different effects on $NH_4V_4O_{10}$ (111) and (110) facets. To investigate the effect of different alkali earth metal nitrate salts, equimolar calcium nitrate and
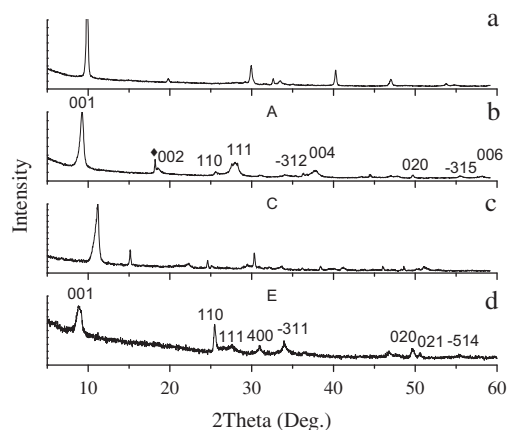

Fig. 1. Wide-angle powder XRD patterns of samples prepared with a different amount of magnesium nitrate (a) 0 g, (b) 0.1 g, (c) 0.2 g and (d) the as-synthesized $NH_4V_4O_{10}$.

strontium nitrate to magnesium nitrate were used to replace magnesium nitrate, $NH_4V_4O_{10}$ were prepared with calcium nitrate under the identical condition in Fig. S1, while an unknown phase was prepared with strontium nitrate in Fig. S2. It can be found that alkali earth metal nitrate salts have different effects on the formation of products, which may be ascribed to different cation radius. Therefore, we succeed in preparing $NH_4V_4O_{10}$ with stronger (111) diffraction peaks than (110) diffraction peaks by addition of magnesium nitrate.

SEM observations show that the as-synthesized sample without the addition of magnesium nitrate is nanoplatelets, as shown in Fig. 2a. The magnified SEM image confirms that the length and width of the nanoplatelet are both around 600 nm in Fig. 2b. As magnesium nitrate was added, the SEM image confirms $NH_4V_4O_{10}$ nanorods in Fig. 2c. The magnified SEM image displays that nanorods have a width of 93–259 nm and a length of 480–5235 nm in Fig. 2d. Micro-flower-like particles consisting of superimposed nano-platelets are observed and displayed for $NH_4V_4O_{10}$ prepared with NH_4NO_3 in Fig. 2e. The diameter of micro-flower-like particles could be up to 13.7 μm. The thickness of platelets is less than 50 nm as estimated from the magnified SEM image in Fig. 2f. When calcium nitrate was used, platelet-like $NH_4V_4O_{10}$ was obtained in Fig. S3. So $NH_4V_4O_{10}$ nanorods can be controllably prepared in the presence of magnesium nitrate.

The sodium intercalation for $NH_4V_4O_{10}$ nanorods and microflowers is also studied by cyclic voltammetry (CV). The CV curves of $NH_4V_4O_{10}$ microflowers without the addition of FEC to electrolyte present two catholic peaks (1.71 V, 2.41 V) and one anodic peak at 2.34 V in Fig. 3a. However, the CV scan of $NH_4V_4O_{10}$ nanorods shows three cathodic peaks at 1.80, 2.23 and 2.49 V as well as three anodic peaks at 2.01, 2.16 and 2.70 V in Fig. 3b. The increasing number of catholic and anodic peaks may be attributed to the improvement of Na-ion insertion and extraction in $NH_4V_4O_{10}$ nanorods for tiny crystalline structure difference. CV was also tested for $NH_4V_4O_{10}$ nanorods after addition of FEC to electrolyte. The first CV curve shows that there are four current peaks for the cathodic scan centered at 1.56, 1.99, 2.25 and 2.44 V in Fig. 3c. Three anodic peaks can also be found at 2.3, 2.73 and 2.95 V. It can also be observed that the value of the current peak for $NH_4V_4O_{10}$ nanorods with the addition of FEC is almost five times higher than that without the addition of FEC. The high current means the better reaction kinetics of Na-ion insertion and extraction in $NH_4V_4O_{10}$ nanorods with the addition of FEC [21]. In other words, the FEC additive makes a great contribution to improve the reaction kinetics of Na-ion insertion and extraction in $NH_4V_4O_{10}$