



Novel hierarchical three-dimensional ammonium vanadate nanowires electrodes for lithium ion battery



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ABSTRACT

Ammonium vanadate ($\text{NH}_4\text{V}_4\text{O}_{10}$) nanowire flowers and nanowires on titanium (Ti) foils are synthesized by hexamethylenetetramine (HMTA)-assisted hydrothermal reactions as a cathode material for lithium-ion battery. The as-prepared $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires are about 50 nm in diameter and several micrometers in length. The effects of reaction time, temperature and additive concentration on the resulting morphology are investigated. Reversible lithium intercalation behavior of the nanowires has been evaluated by cyclic voltammetry and galvanostatic discharge-charge cycling. The $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires on Ti foil deliver a high discharge capacity of $168.5 \text{ mA h g}^{-1}$ after 100 cycles between 2.0 and 4.0 V at 50 mA g^{-1} . A high rate capability is obtained with a remaining discharge capacity of about $182.6 \text{ mA h g}^{-1}$ after 35 cycles at various rates. Further, the $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires on Ti foil have a higher discharge capacity of $330.5 \text{ mA h g}^{-1}$ after 100 cycles at 0.8–4.0 V at 50 mA g^{-1} .

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1. Introduction

Vanadium oxides and their derivative compounds have received significant attention recently because of their distinctive structural versatility and novel applications in electric field-effect transistors, chemical sensors/actuators, catalysis, high-energy lithium batteries and electrochemical devices [1–8]. V_2O_5 one of vanadium oxides is considered to be a layered structure, in which VO_5 square pyramids are connected by sharing vertices and edges, and thereby, forming individual layers [9,10]. The interactions between these layers are rather weak, as indicated by the exceptionally long V–O distance [11]. This layer structure particularity permits the synthesis of the bronze phase $\text{M}_x\text{V}_y\text{O}_z$ (M: Li, Na, K, Cs, Ca, Ag, etc.) with various metal cations embedded between the layers without a far-reaching restructuring [12,13]. The layered lithium trivanadate ($\text{Li}_x\text{V}_3\text{O}_8$) can accommodate more than four lithium-ions (Li^+), giving rise to $372.5 \text{ mA h g}^{-1}$ theoretical capacity [14]. Other cations like Na^+ and NH_4^+ rather than lithium are used to bridge

(V_3O_8)-layers, which can accommodate fairly large number of Li^+ [15]. Such Na^+ or NH_4^+ cation-layered $\text{M}_x\text{V}_3\text{O}_8$, with a larger interlayer spacing, has the potential to be used as major lithium-battery cathode materials since both ammonium and sodium are abundant in earth core and less expensive. The large interlayer spacing can improve the Li^+ motion (electrode kinetics) within the lattice drastically, enhancing the electrode rate performance. Recently, another class of ammonium vanadate ($\text{NH}_4\text{V}_4\text{O}_{10}$) (also written as $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$) based material was introduced in the literature, which is similar to $\text{NH}_4\text{V}_3\text{O}_8$ or V_2O_5 materials. In the $\text{NH}_4\text{V}_4\text{O}_{10}$ structure, NH_4^+ ions are intercalated between two bilayer of V_2O_5 , resulting higher electronic conductivity and lithium diffusion coefficient as compared with V_2O_5 cathode [16,17]. $\text{NH}_4\text{V}_4\text{O}_{10}$ is a potential electrode material with a high electrochemical performance [18–22]. For instance, Zhang et al. [19] have prepared $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts with an initial discharge capacity of $171.8 \text{ mA h g}^{-1}$ at a current rate of 12.5 mA g^{-1} and Wang et al. [1] have reported the synthesis of $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts with initial discharge capacity of $225.2 \text{ mA h g}^{-1}$ at 15.0 mA g^{-1} current rate. The impact of binder on stable high rate electrochemical performance of $\text{NH}_4\text{V}_4\text{O}_{10}$ was studied by Sarkar et al. [20] and it was found that carboxy methyl cellulose based cathode delivers superior

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capacity. Ren et al. [22] prepared flower-like $\text{NH}_4\text{V}_4\text{O}_{10}$ micro-nano structures which exhibited high discharge specific capacity of 307 mA h g^{-1} at a current rate of 12.5 mA g^{-1} .

Nanosized electrode material can provide not only shortened diffusion pathways for lithium-ion intercalation/de-intercalation in the host material, but also high specific surface areas for larger effective contact with electrolyte to produce stronger Li^+ flux crossing the interfaces [8,10,23,7]. Hydrothermal method has been widely used to synthesize lithium intercalation materials with various nanomorphologies (nanorods, nanowires and nanospheres, etc.) [24–26]. In the present work, we describe a facile largescale hydrothermal method to fabricate $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowire flowers and nanowires on titanium (Ti) foils, respectively. The effects of the reaction time, temperature and additive concentration on the resulting structure are investigated. Further, electrochemical behavior of the nanowires has been evaluated by cyclic voltammetry and galvanostatic discharge-charge cycling.

2. Experimental

2.1. Materials and methods

In a typical synthesis route, the 40 mL mixed solution of NH_4VO_3 (0.12 mol L^{-1}) and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.24 mol L^{-1}) was added into a 50 mL Teflon container, followed by addition of hexamethylenetetramine (0.02 mol L^{-1}) with stirring. A piece of Ti foil (99.5% purity) was placed into the container. Then the container was sealed in an autoclave and transferred to an electrical oven to keep at 100, 120, 150 °C for different times (20 min, 30 min, 40 min, 1 h and 2 h). After cooling down naturally, the substrate was taken out from the container and the powders were collected by centrifugal separation, washed with pure ethanol for three times, and then dried at 60 °C for 24 h. The sample on substrate fabricated at 100 °C, 120 °C and 150 °C is named $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires-100 °C, $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires-120 °C and $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires-150 °C, respectively.

2.2. Materials characterization

X-ray diffraction analyses of the samples were performed using an X-ray diffractometer (XRD, D/MAX2500, Rigaku) with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Thermogravimetric (TG) analysis of the precursor powders were conducted using simultaneous thermal analyzer (STA, NETZSCH, Germany) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The morphology of the samples was characterized by scanning electron microscopes (SEM, JEOL JSM-6300 and JSM-6360LV). For SEM sample preparation, a thin Au layer ($\sim 3 \text{ nm}$) was sputter coated to form a conducting film on sample surface for observation. Raman spectra were recorded at room temperature using a Renishaw Micro-Raman spectrometer. An Nd:YAG laser (532 nm) was used as the excitation source. Transmission electron microscopy (TEM) images were taken on JEOL-2100F at an accelerating voltage of 200 kV. The chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, KAlpha 1063, Thermo Fisher Scientific, UK).

2.3. Electrochemical measurements

The $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires on Ti foil dried in a vacuum oven at 120 °C were used as the working electrode. For $\text{NH}_4\text{V}_4\text{O}_{10}$ powder, the working electrode slurry was prepared by dispersing $\text{NH}_4\text{V}_4\text{O}_{10}$, acetylene black and poly-(vinylidene fluoride) (PVDF) binder in an *N*-methylpyrrolidone solution at a weight ratio of 80:10:10. The slurry was spread on aluminum foil disks and dried in a vacuum oven at 120 °C prior to form coin-like cell

assembly. Lithium foil was used as the counter and reference electrode, and 1.0 M LiPF_6 in ethyl carbonate/dimethyl carbonate (1:1 volume ratio) was used as the electrolyte. Cyclic voltammetry measurements were performed on an AUTOLAB electrochemical workstation (PG302N). Galvanostatic charging/discharging was conducted on a battery tester (Land CT2001).

3. Results and discussion

The morphologies of the as-prepared dark-green powders and nanostructures grown on Ti foil were investigated using SEM, as shown in Fig. 1. Uniform hairy ball-like spheres, with about $8 \text{ }\mu\text{m}$ in diameter, are observed in the powders, as shown in Fig. 1(a). Each single hairy ball-like sphere is composed of nanowires growing outwards along the radial direction with a common center, as shown in the magnified image in Fig. 1(b). Fig. 1(c) and (d) reveals the nanowires grown on the Ti foil surface vertically. The diameter of the nanowires is about 50 nm, and the length, about several microns, as shown from the cross-section view in Fig. 1(e). The TEM images are shown in Fig. S1 (Support information). The XRD pattern of the as-prepared sample is presented in Fig. 1(f). All of the diffraction peaks are perfectly indexed as monoclinic $\text{NH}_4\text{V}_4\text{O}_{10}$ (PDF no. 31-0075) with lattice parameters $a = 11.71 \text{ \AA}$, $b = 3.66 \text{ \AA}$, $c = 9.72 \text{ \AA}$ and $\beta = 101^\circ$. No impurities, such as V_2O_5 or VO_2 , can be detected in this pattern, indicating that pure $\text{NH}_4\text{V}_4\text{O}_{10}$ was obtained using the current synthesis conditions [27]. Furthermore, the TG result is shown in Fig. S2 (Support information) [27]. The Raman spectrum of the $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires is presented in Fig. 1(g), which exhibits 10 bands in the $100\text{--}1200 \text{ cm}^{-1}$ frequency range, located at 140.6, 191.0, 281.0, 404.7, 475.7, 520.8, 691.7, 876.4, 926.1 and 991.0 cm^{-1} . For V_2O_5 , the local environment of the vanadium atom leads to the existence of four types of vanadium-oxygen bonds (V-O bond lengths d_1 to d_4 vary from 1.58 to 2.02 Å) [28]. Due to the difference in bond lengths, the spectral lines characteristic for the bond-stretching oscillations of the different V-O bonds can be assigned. Further, bending vibrations of the V-O-V angle and O-V-O angle yield different characteristic lines. The bond-stretching modes cover the interval of $500\text{--}1000 \text{ cm}^{-1}$ and the angle-bending modes cover the $200\text{--}500 \text{ cm}^{-1}$ range [29]. In the crystal structure of $\text{NH}_4\text{V}_4\text{O}_{10}$, VO_5 tetragonal pyramids connect together to build each layer and NH_4^+ ions insert into the space between the layers, which a structure is similar to the layered V_2O_5 [22]. The bands in Fig. 1(g) are attributed to the bond-stretching modes of V-O and the angle-bending modes of the V-O-V angle or O-V-O angle.

The morphologies of the products at different reaction times on Ti foil were also examined. Fig. 2 shows representative SEM images of the samples, which were collected stepwise after 20 min, 30 min, 1 h and 2 h of reaction, respectively. After 20 min of reaction time, the Ti foil was coated with a irregular particles layer (Fig. 2(a)). In the sample produced in 30 min of reaction time, fan-shaped nanowires aggregates were appeared on the surface of the Ti foil (Fig. 2(b)). In the sample with 40 min reaction time, the nanowires were further assembled on the surface of Ti foil, as shown in Fig. 1(c). After 1 h of reaction time (Fig. 2(c)), the spaces among the nanowires were cross-linked to form thin film-like structures, and this phenomenon was further evidently presented after 2 h (Fig. 2(d) and (e)). A schematic representation of the morphological evolution process of the $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires on Ti foil is presented in Fig. 2(f). At 20 min, irregular particles were coated on the foil which are the reactive sites to grow nanowires. After 30 min of reaction time, fan-shaped nanowires aggregates were formed from the as-prepared particles. In the products in 40 min of reaction time, the nanowires grow longer. After 1 h or 2 h of reaction time, the nanowires crosslinked and thin film structures were formed. The

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