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Three-dimensional $Zn_3V_3O_8$/carbon fiber cloth composites as binder-free anode for lithium-ion batteries

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ABSTRACT

Ternary metal vanadium oxides have been considered as potential anode materials for lithium-ion batteries (LIBs). However, the poor electronic conductivity and large volume expansion during the discharge/charge process lead to poor electrochemical performance. Herein, we firstly report the preparation of grass-like $Zn_3V_3O_8$ nanobelts array coated 3D carbon fiber cloth ($Zn_3V_3O_8$/CFC) as a binder-free anode for LIBs. The composites could effectively improve the kinetics of electronic transportation and mitigate the volume expansion of electrodes during discharge/charge process. As a result, the $Zn_3V_3O_8$/CFC exhibits excellent Li^+ storage properties. It can deliver a reversible capacity of $\sim$1750 mA h g^{-1} at a low current density of 100 mA g^{-1} and a specific capacity of 942 mA h g^{-1} at the high rate of 1.5 A g^{-1}. Even measured at high current density of 5 A g^{-1}, the electrode could maintain a high capacity of 455 mA h g^{-1} after 500 cycles with a capacity retention of 82.7%.

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1. Introduction

Due to the global energy crisis and environmental deterioration, the demands for clean energy are particularly urgent [1–4]. The lithium-ion batteries (LIBs), one of the most important energy storage devices, have been the prime candidate for a range of applications, such as portable electronics, electric vehicles (EV) and hybrid electric vehicles (HEV), because of their high energy density, low-cost, long cycle life and environmental benignity [5–8]. Mixed transition metal oxides (MTMOs) have been extensively investigated as anode materials due to their near triple theoretical capacity of the commercial graphite (372 mA h g^{-1}). Particularly, MTMOs with different metal cations exhibit excellent electrochemical activities owing to their complex chemical composition, interfacial effects and synergistic effects of multiple metal species [1,3,4,7,9–13]. Recently, metal vanadates ($A_xV_yO_z$, A = Fe, Co, Ni, Cu, Zn, Mn, etc.) have been considered as promising electrodes because of their particular properties [9,14–20]. For instance, they could be easily prepared due to multiple valence states of vanadium [16,17]. Furthermore, with the formation of amorphous VO_x matrixes during electrochemical process, agglomerations of other metal species could be effectively prevented [21,22].

Among various metal vanadate anodes, zinc vanadium oxides ($Zn_xV_yO_z$) have attracted great attention since they possess many advantages, such as high specific capacity, low cost, easily available and low environmental pollution [14,23–25]. For example, ultra-long monoclinic ZnV_2O_6 nanowires prepared by Sun's group can deliver 972.9 mA h g^{-1} at 100 mA g^{-1} [14]. Gan et al. reported $Zn_3V_2O_8$ nanosheets which delivered the capacity triple than the commercial graphite anode (372 mA h g^{-1}) [15]. Nevertheless, they still suffer from poor electronic conductivity and large volume expansion during the discharge and charge process, which greatly impede their further application as anodes for LIBs [8,22,26–28].

An effective way to overcome the above issues is to combine the $Zn_xV_yO_z$ nanostructures with three-dimensional (3D) electro-conductive substrates, due to their high electrical conductivity, large surface areas and more active sites [29–34]. Constructing 3D hierarchical architectures is also beneficial for electrolyte penetration and alleviating volume expansion of active materials. Carbon fiber cloth (CFC) as one kind of 3D flexible substrates is widely used in LIBs [35–39]. For example, Liu and his colleagues reported $ZnCo_2O_4$/CFC composites as anode for flexible lithium-ion batteries, which hold good electrochemical performance. These active materials/CFC composites as high-performance binder-free

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anodes demonstrate great potential for the next generation of LIBs. However, to date, there is no report involved in synthesis of 3D $Zn_xV_yO_z$/CFC composites with various applications.

In this work, we firstly report a facile and efficient way to prepare 3D grass-like $Zn_3V_3O_8$ nanobelts array coated CFC composites as a binder-free anode for LIBs. The construction of 3D electrode has the following advantages. Firstly, 3D flexible CFC current collectors replace traditional metal current collectors (such as copper and aluminum foil), providing excellent mechanical strength, high electrical conductivity, outstanding corrosion resistant property and available commercially. Secondly, grass-like $Zn_3V_3O_8$ directly grown on CFC as binder-free anode significantly reduces inactive interface. Lastly, the 3D structure can also effectively suppress the volume expansion of $Zn_3V_3O_8$ during the charge and discharge process. As a result, $Zn_3V_3O_8$/CFC electrodes display high specific capacity, excellent rate capability and good cycling performance.

2. Experimental Section

2.1. Materials synthesis

The $Zn_3V_3O_8$/CFC composites were prepared by a facial hydrothermal method. Firstly, 1 mmol $Zn(NO_3)_2{\cdot}6H_2O$ crystals were dissolved into 5 ml of de-ionized water to form 0.2 M transparent $Zn(NO_3)_2$ solution. Secondly, 1 mmol vanadium pentoxide (V_2O_5) were dispersed into 25 ml de-ionized water, followed by adding 2 ml of H_2O_2, and under magnetic stirring until forming a bright-orange solution. Then, the $Zn(NO_3)_2$ solution was slowly added into the bright-orange solution with continuous stirring for a few minute, and then the obtained mixture was transferred into the 50 ml Teflon-lined autoclave with a piece of carbon fiber cloth (2 cm × 2 cm), which was sealed and heated under 200 °C for 48 h. The carbon cloth substrates were previously washed by sonication in acetone, deionized water and ethanol for 20 min, respectively. After heating, the autoclave liners were cooled down to room temperature naturally. The carbon fiber cloth coated with green products was washed by de-ionized water and ethanol for several times to remove the byproduct, and then dried at 60 °C for 12 h. After annealing at 600 °C in argon atmosphere for 2 h, the finally sample were obtained. The $Zn_3V_3O_8$ powders were obtained with the similar method but without adding carbon cloth substrates.

2.2. Characterization

The crystallographic information of the samples were characterized by X-ray diffraction (XRD) measurements (Rigaku D/max 2500 X-ray diffractometer with non-monochromated Cu-Kαradiation, λ = 1.54178 Å). The microscopic morphology of the samples was examined by field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM 230, 20 kV) and transmission electron microscopy (TEM, JEOL JEM-2100 F, 200 kV).

2.3. Electrode fabrication and electrochemical measurements

A CR2016-type coin cell was assembled in a glove box (Mbraun, Germany) filled with ultra-high pure argon gas, which use lithium foil as the counter electrodes, polypropylene membrane as the separator, and 1.0 M solution of $LiPF_6$ in ethylene carbonate(EC)/diethyl carbonate(DEC)/dimethyl carbonate(DMC) (1:1:1, by volume) as electrolyte. The $Zn_3V_3O_8$/CFC composites (the loading mass of $Zn_3V_3O_8$ active materials is ~1.3 mg cm^{-2}, ~10 wt% of $Zn_3V_3O_8$/CFC) were directly used as the working electrodes. The cells were first aged for 8 h before test to ensure full absorption of the electrolyte into the electrodes. Cyclic voltammetry was tested on an electrochemical workstation (CHI600C) in the voltage range of 0.01–3 V (vs. Li/Li^+). The electrochemical impedance spectroscopy (ESI) measurements were performed on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co., Germany) in the frequency range from 100 kHz to 0.01 Hz. The galvanostatic charge/discharge performances of the electrodes were studied at ambient temperature in a potential range of 0.01–3 V vs Li/Li^+ with a multichannel battery testing system (LAND CT2001A, China).

3. Results and discussions

Fig. 1 shows the schematic illustration of synthetic process of the $Zn_3V_3O_8$/CFC. Firstly, the carbon cloth was uniformly covered by the grass-like Zn-V-alkoxide nanobelts precursor. After the annealing process in argon atmosphere with the heating rate of 1 °C/min, the $Zn_3V_3O_8$/CFC composites were obtained. The morphology features of $Zn_3V_3O_8$/CFC composites were investigated by FESEM. The low-magnification FESEM image (Fig. 2a) clearly shows that each carbon fiber was uniformly covered by precursor nanobelts. We can see from Fig. 2b that these nanobelts with ~20 nm in diameter and ~500 nm in length orderly arranged on CFC. After annealing process, the grass-like morphology can be well-maintained (Fig. 2c). These nano-sized grass-like nanobelts could shorten the diffusion ways of lithium ions and offer enough space for lithium ions to access and transport. The CFC as 3D conductive substrate could effectively improve the charge transfer and benefit in against the aggregation and volume expansion of the active materials during the process of lithiation/delithiation.

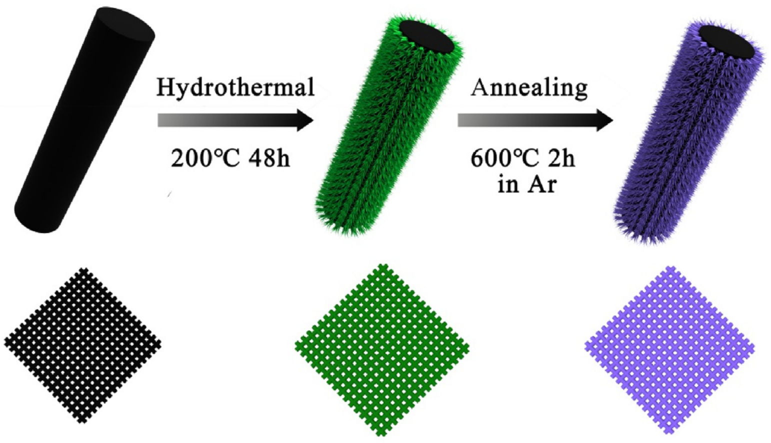

Fig. 1. Schematic illustration of synthetic process of $Zn_3V_3O_8$/CFC.

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