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Cobalt-doped V_2O_5 nanowire arrays on Ti foil for enhanced lithium-ion storage

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ABSTRACT

Cobalt (Co)-doped V_2O_5 nanowire arrays are prepared using a simple hydrothermal method by controlling appropriate molar ratios of cobaltous acetate ($Co(CH_3COO)_2 \cdot 4H_2O$) and ammonium vanadate (NH_4VO_3). The products are characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy and Fourier-transform infrared spectroscopy. The nanowires are identified as cobalt-doped V_2O_5 when the molar ratio of cobalt/vanadium precursors is less than 0.064 (calculated from raw materials); while as the molar ratio increases to 0.128, the nanowires are composed of a mixture of V_2O_5 and Co_3O_4. The valence states of Co, O and V are tested by X-ray photoelectron spectroscopy, and the distribution of these elements is confirmed by elemental mapping. The prepared samples are studied and compared with their lithium-storage properties using cyclic voltammetry, charge-discharge test and rate performances. The Co-doped V_2O_5 nanowires have a higher electrochemical lithium-storage capacity than that of the mixed V_2O_5/Co_3O_4 nanowires. At a current density of 30 mA g^{-1}, an initial discharge capacity of 624.64 mAh g^{-1} is achieved in a voltage range of 2–4 V.

1. Introduction

Although traditional fossil energy resources, particularly coals, can barely satisfy the peoples' power demands, their environmental pollution and CO_2 emissions have seriously impacted human survivals [1]. It is very urgent to find new clean energy resources to replace the fossil fuels. As a clean and renewable energy source, electric energy, especially when using lithium-ion battery, has the advantages of low cost, less pollution and being renewable.

Vanadium is one of the most abundant elements in the earth's crust [2–5], with four oxidation states of V^{2+}, V^{3+}, V^{4+} and V^{5+}, which are associated with oxides of VO, V_2O_3, VO_2 and V_2O_5, respectively. These oxides usually co-exist in combined oxidation states with complicated crystalline structures. Because the vanadium pentoxide (V_2O_5) is the most common oxide of vanadium, it can be prepared at a low cost and is widely used in different fields, such as in lithium-ion batteries [6–10] and supercapacitors [11–15]. It has an orthorhombic unit cell, which is made up of bilayers consisting of stacks of distorted VO_5 square pyramids that share edges to form zigzag double chains [16,17].

Because the bulky V_2O_5 suffers from poor structural stability, low Li^+ diffusion coefficient (10^{-14}–10^{-12} $cm^2\,s^{-1}$) and moderate electric conductivity (10^{-7}–10^{-6} S cm^{-1}), poor cycling and rate capabilities are resulted [18,19]. In order to overcome these drawbacks, nanotechnology was adopted by researchers to fabricate a series of V_2O_5 nanostructures, including 0 dimensional (0D) nanoparticles, 1D nanowires, 2D nanosheets and 3D hierarchical nanomaterials via different ways including hydrothermal treatment, electrodeposition, vapor deposition, electrospinning, spray pyrolysis, and atomic layer deposition, etc. [20–27]. However, its capacity still decreased during the initial cycles and its morphology and single-crystal structure could be destroyed quickly.

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Due to the low capacity retention and poor rate capability of V_2O_5, it is still a major challenge in actual use of V_2O_5 [28–35]. These long-time problems have been partly ascribed to the large volume changes during repeated insertion and removal of lithium ions from the electrode, resulting in localized stress and eventually electrode failure; and the polymer/gel layer and the solid electrolyte interface (SEI) are also formed because of the catalytic degradation of the electrolyte [35,36]. Generally, acceptable methods to abate these problems included hybridization [37], and building core/shell structure [38,39]. Indeed, there are increasing evidences showing that carbon hybridization, core/shell configuration and tailored nanostructured materials can remarkably enhance the electrochemical properties compared to their counterparts [40–50]. For example, V_2O_3/CNTs hybrid [37] and V_2O_5/conductive-polymer core/shell configuration [38] have exhibited high rate capabilities [46].

The electrochemical performance of the electrode materials can be improved by doping transition metal ions to enhance their inherent conductivity [51–58]. Particularly, cationic doping has been identified as an effective way to ameliorate the electrical conductivity and charge transfer capability of the electrode materials. Motivated by these interests, various metal cations such as antimony [43], niobium [58], tantalum [59,60], cobalt (Co) [53,61], copper [62–64], yttrium [65], aluminium [66], titanium [67] and manganese [68] have been intensely used to improve the electrochemical performance of metal oxide materials. Among various ions, few researches focus on Co doping in V_2O_5, though Co doping has been used for enhancing the electrochemical performance of cathode materials for lithium-ion battery [69], such as lithium iron phosphate ($LiFePO_4$). In addition, Co doping has shown to be advantageous in $LiNiO_2$ [70–72], $LiMnO_2$ [73] and other Li-based materials. High-level Co doping of $LiFePO_4$ shows a negative impact on property, while low-level Co doping of $LiFePO_4$ presents a detectable improvement of the capacity [74].

In this work, Co-doped V_2O_5 nanowire arrays were prepared by a hydrothermal method by adding different amount of $Co(CH_3COO)_2 \cdot 4H_2O$ into the reaction solution. The structure and morphologies of the samples were tested and compared in details. As electrodes of lithium-ion battery, Co-doped V_2O_5 showed excellent capacity, great cycling performance and high rate capability. It is for the first time to report Co-doped V_2O_5 nanowire arrays as electrode materials for lithium-ion battery.

2. Experimental section

2.1. Synthesis of Co-doped V_2O_5 & Co_3O_4/V_2O_5 on Ti substrate

Chemicals of 1.17 g of ammonium vanadate (NH_4VO_3), 2.52 g oxalate acid ($H_2C_2O_2$), 0.28 g hexamethylenetetramine ($C_6H_{12}N_4$) and 0.04 g cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$) was dissolved in 17.5 ml distilled water to form a homogeneous transparent solution after long stirring. The solution was transferred into a 20 ml Teflon-lined stainless steel autoclave. Ti foils were burnished with a fine sand paper. Then the Ti foils were cut into the diameter of the circle (1 cm) and ultrasonically degreased in ethanol at room temperature for 30 min. Next, a Ti foil was dipped into the Teflon-lined autoclave, which was then sealed and maintained at 150 °C for 1 h, followed with cooling in furnace naturally. The final products were collected and rinsed with ethanol and deionized water, and dried at 80 °C in air. Finally, the obtained precursor was calcined at 200 °C for 2 h with a heating rate of 1 °C min^{-1} in air. The amount of active material loaded was approximately 2–3 mg cm^{-2}, which was determined by the mass difference before and after growing the nanowires. For comparison, a series of experiments were carried out by controlling the molar ratio of Co $(CH_3COO)_2 \cdot 4H_2O/NH_4VO_3$ from 0 to 0.016, 0.064, 0.128, 0.256 and 0.512 into the reaction solution, and these samples are denoted as Co*0, Co*1, Co*4, Co*8, Co*16 and Co*32, respectively.

2.2. Sample characterization

X-ray diffraction (XRD) analysis of the samples was performed using an X-ray diffractometer (D/MAX2500, Rigaku) with Cu K_α radiation ($\lambda = 1.5418$ Å). The surface morphology of the samples was characterized by scanning electron microscopy (SEM) using JEOL JSM-6300 and JSM-6360LV. Transmission electron microscopy (TEM) was done using JEOL-2100F with an accelerating voltage of 200 kV. The chemical composition of the sample was analyzed by X-ray photoelectron spectroscopy (XPS) using KAlpha 1063 (Thermo Fisher Scientific, UK). The Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using a Nicolet 6700 FTIR spectrometer.

2.3. Electrochemical measurements

The electrochemical tests for lithium-ion batteries were carried out using CR2016 coin cells. 1 M $LiPF_6$ (EC: DMC: EMC = 1: 1: 1, in volume) solution was used as electrolyte for the half cells with Li metal as counter electrode. The cells were assembled in a glovebox (Mbraun, LabMaster 100, Germany) under an argon atmosphere

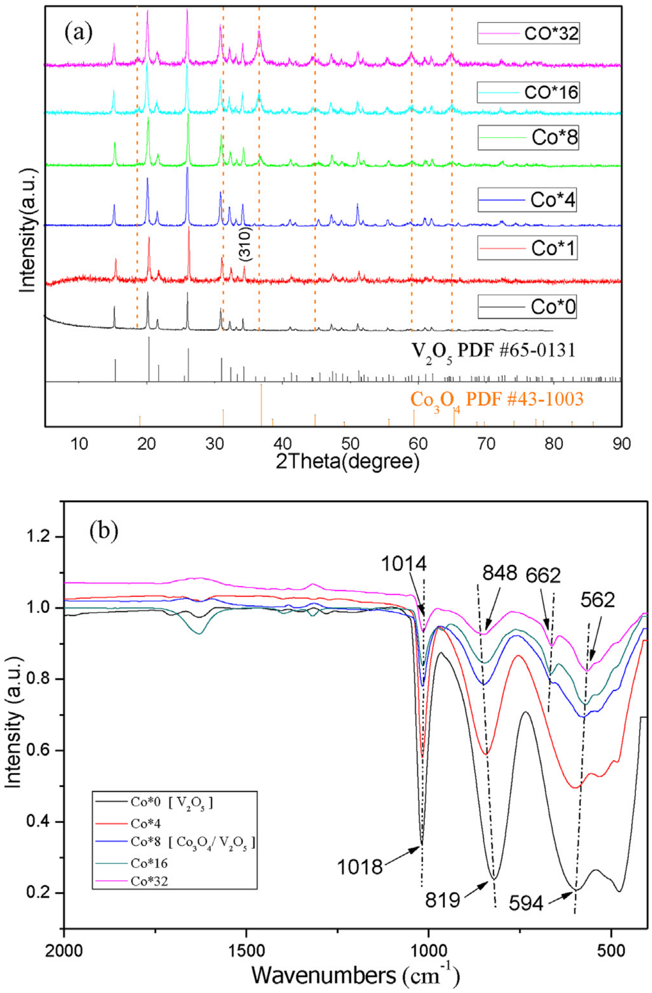

Fig. 1. Typical XRD patterns (a) and FTIR spectra (b) for the pure V_2O_5, Co-doped V_2O_5 and mixed Co_3O_4/V_2O_5 nanowires.