Facile synthesis of $Co_3V_2O_8$ nanoparticle arrays on Ni foam as binder-free electrode with improved lithium storage properties

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ARTICLE INFO

ABSTRACT

The $Co_3V_2O_8$ nanoparticle arrays on Ni foam were synthesized by a simple one-step procedure using a low-temperature hydrothermal method. This architecture consisted of ultrafine $Co_3V_2O_8$ nanoparticles with a mean size of 30–60 nm, which covered homogeneously onto the porous Ni foam, forming a uniform film-like morphology. The $Co_3V_2O_8$ nanoparticles not only provided sufficient electro-active interactions for Li-storages reaction, but also had good mechanical contact with the Ni foam, hence improving reaction kinetics and enhancing electrode integrity. When used as a new sort of binder-free anode for Li-ion batteries (LIBs), this unique electrode delivered high initial discharge capacity of 1586.9 mA h g^{-1} at 200 mA g^{-1} and retained at 1289 mA h g^{-1} after 100 cycles, and the discharge capacity maintained at 1004.4 mA h g^{-1} after 800 cycles at 500 mA g^{-1}. Even when the current was 10 A g^{-1}, discharge capacity of 471.4 mA h g^{-1} could be achieved. In addition, the charge/discharge mechanism of $Co_3V_2O_8$ based on conversion and intercalation reaction routes were verified by *ex-situ* XRD diffraction. Therefore, the $Co_3V_2O_8$ nanoparticle arrays on Ni foam might open a new insight for transition metal oxides as electrode materials for LIBs.

1. Introduction

Nowadays, recharge Li-ion batteries (LIBs) are considered the dominant power sources of most portable electronics and electric vehicles owing to their high energy density, long lifespan and environmental friendliness [1]. However, the current commercial graphite electrodes cannot meet the growing requirement of high energy/power density due to their low specific capacity (372 mA h g^{-1}). Hence, it is high desirable to develop high-performance alternative anode materials for LIBs [2,3]. Due to the much higher theoretical capacity over the commercially used graphite, transition metal oxides (TMOs) have been regarded as promising anode materials in LIBs [4]. In particular, cobalt-based oxides have attracted considerable interest due to their high capacity, good chemical/thermal stability, and low cost synthesis [5,6]. However, their practical application is largely restrained by the low electrical conductivity, poor cycle stability and large volume expansion during the charge/discharge process [7,8].

To solve these problems, the first strategy is to design nanostructured materials [9,10], such as nanoparticles [11], nanowires [12], and nanosheets [13] because they can alleviate pulverization strain caused by the Li-ion insertion/extraction and avoid rapid capacity fading [14].

Among various nanostructures, zero-dimensional (0 D) nanoparticles stand out because of reduced Li-ion diffusion pathways and the abundant electro-active interactions for Li-ion storage [15]. Meanwhile, the small sized and uniform distribution of the nanoparticles can accommodate volume variation and decrease the aggregation of active materials in cycling for maintaining the stable structure [16,17]. The second approach is to grow active materials directly on conductive collectors, which can enhance their electronic conductivity and structure stability, leading to improved electrochemical performance [18–21]. Especially, the Ni foam has porous architecture with large surface area, good electronic conductivity and structure stability, which can be used as an ideal deposition substrate [22–24]. Another effective strategy is to design various binary metal oxides [25], which can synergistically improve reversible capacity, electrochemical stability and rate capability of single metal oxides in view of their enhanced redox activity and electrical conductivity. In this case, the cobalt-based binary metal oxides, such as $NiCo_2O_4$ [26], $CuCo_2O_4$ [27], Co_2GeO_4 [28], $CoMo_2O_4$ [29] and CoV_2O_6 [30], have shown attractive electrochemical performance as anode materials for LIBs. Among them, $Co_3V_2O_8$ has a wide range of applications in supercapacitors [31] and catalysis [32]. As a new sort of anode, cobalt vanadium oxide, $Co_3V_2O_8$, shows superior electrochemical activities, which may have potential

application in LIBs. For example, Yang et al. reported the fabrication of $Co_3V_2O_8$ multilayered nanosheets by hydrothermal method at 180 °C for 12 h followed by annealing in air at 350 °C for 2 h, which showed remarkable specific capacities (1114 mA h g^{-1}) after 100 cycles [33]. The Li storage mechanism of $Co_3V_2O_8$ was also studied in that study, involving in a conversion reaction ($CoO+2Li^++2e^- \leftrightarrow Co+Li_2O$, $Co^{2+} \leftrightarrow Co°$), and a partial redox reaction ($Li_xV_2O_5+yLi^++ye^- \leftrightarrow Li_{x+y}V_2O_5$, $0 < x+y < 4$, $V^{5+} \leftrightarrow V^{4+} \leftrightarrow V^{3+}$). The amount of lithiation/delithiation was calculated to be 6−10 Li$^+$ per formula unit for the $Co_3V_2O_8$, showing a range of the theoretical specific capacity from a low of 394.7 to a high of 657.9 mA h g^{-1}. The $Co_3V_2O_8$ interconnected hollow microspheres were synthesized by Luo et al. through the combination of hydrothermal synthesis at 180 °C for 24 h and subsequent annealing treatment at 450 °C for 10 h [34]. After 300 cycles at a high current density of 10 A g^{-1}, it delivered a reversible capacity of 424 mA h g^{-1}. In addition, Gao et al. synthesized mesoporous $Co_3V_2O_8$ nanoparticles grown on reduced graphene with a size of about 100 nm by a hydrothermal method at 120 °C for 6 h and post-calcination at 450 °C for 10 h in air [35]. It showed the initial capacity of 1381.5 mA h g^{-1} and the capacity retention was 1050 mA h g^{-1} over 200 cycles at a current density of 50 mA g^{-1}. Obviously, the synthesis methods of the $Co_3V_2O_8$ in their studies required a complicated two-step process and high reaction temperature, making the development of nanostructured $Co_3V_2O_8$ time-consuming and energy-intensive. Therefore, to seek cheap and mild synthetic strategies is of great significant to fabricate $Co_3V_2O_8$ with unique nanostructure and enhanced energy storage performances. Furthermore, the direct growth of well- distributed $Co_3V_2O_8$ nanostructures on porous substrates has not been realized until now.

In this work, we synthesized $Co_3V_2O_8$ nanoparticle arrays (NPAs) on Ni foam by a simple one-step and low-temperature (90 °C for 3 h merely) hydrothermal method. The ultrafine $Co_3V_2O_8$ nanoparticles were uniformly grown on porous Ni foam without obvious agglomeration. As a binder-free anode for LIBs, this electrode showed improved electrochemical performances including high specific capacity, superior cycling stability and excellent rate capability due to the ultrafine $Co_3V_2O_8$ nanoparticles structure in intimate contact with the Ni foam, which offered enhanced electrical/ionic transport and structure stability. In addition, the charge/discharge mechanism of $Co_3V_2O_8$ also was also investigated by *ex situ* XRD, which makes contributions to the TMOs applied for LIBs.

2. Experimental sections

2.1. Synthesis of materials

All chemicals used in this work were of analytical grade, which were purchased from Sinopharm Chemical Reagent Co. Ltd, and doubly distilled water was used throughout the experiment. The Ni foam was cleaned using 1 M HCl, ethanol, acetone and water to remove impurities on the surface of the substrates. The $Co_3V_2O_8$ NPAs on Ni foam was prepared as follows. 3.38 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 2.24 mmol $Na_3VO_4 \cdot 12H_2O$ were dissolved into 80 mL deionized water at room temperature, then the obtained mixed solution was transferred into a 100 mL Teflon-lined autoclave with insertion of a piece of clean Ni foam, and maintained at 90 °C for 3 h. After that, the resultant samples were washed with distilled water and absolute ethanol several times, and dried at 200 °C for 12 h under vacuum. For comparison, sediment ($Co_3V_2O_8$ powders) in the solution was also collected.

2.2. Materials characterization

Crystal structures of the samples were determined with X-ray diffraction (XRD using D/MAX 2400 diffractometer). The morphology and microstructure were characterized by the Scanning Electron Microscopy (SEM; JEOL, JSM-6701F, 15 kV) with Energy Dispersive Spectrometer (EDS) and the Transmission Electron Microscope (TEM, JEOL, JEM-2010). Inductively Coupled Plasma (ICP-AES, IRIS Intrepid II XSP) was employed to measure the element component.

2.3. Electrochemical measurements

The electrochemical properties were tested using CR-2032 coin-type cells. The $Co_3V_2O_8$ NPAs on Ni foam directly acted as working electrode. The mass loading of the active materials was around 1−2 mg cm^{-2}. A Li foil was used as both the counter electrode and the reference electrode. The used electrolyte was 1 M LiPF$_6$ in ethylene carbonate and dimethyl carbonate (1:1, by volume). The cells were cycled using a Li-ion batteries cycler (LAND CT2001A) in the voltage window 0.01−3 V (vs. Li$^+$/Li) at different current rates. Cyclic voltammetry (CV; 0.01−3 V, 0.01 mV s^{-1}) and Electrochemical impedance spectroscopy (EIS; 100 kHz−0.01 Hz, 5 mV/s) of the cell was performed on the electrochemical workstation (CHI660C). For comparison, the $Co_3V_2O_8$ powders electrodes were fabricated by mixing the $Co_3V_2O_8$ powders, acetylene black and a sodium alginate at a weight ratio of 70:20:10.

3. Results and discussion

3.1. Synthesis and characterization

The crystal structure of the as-prepared $Co_3V_2O_8$ NPAs on Ni foam was analyzed by XRD. As shown in Fig. 1a, the diffraction peaks located at 15.1, 24.0, 26.3, 30.4, 32.3, 34.1, 35.7, 40.0, 40.6, 57.6, 59.6, 60.9
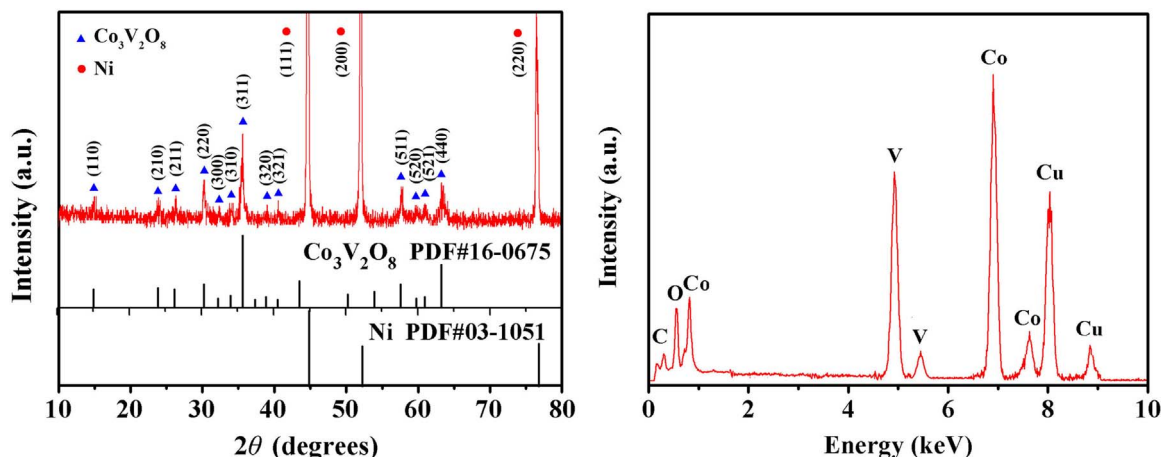

Fig. 1. (a) XRD patterns of $Co_3V_2O_8$ nanoparticle arrays on Ni foam. (b) The EDS spectrum of $Co_3V_2O_8$ nanoparticle arrays on Ni foam.