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Effect of polyethylene glycol on vanadium oxide nanotubes in lithium-ion batteries

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ABSTRACT

Vanadium oxide (V_2O_5) nanotubes and polyethylene glycol (PEG) surfactant V_2O_5 nanotubes were synthesized using simple hydrothermal process. The electrochemical performance of these nanostructures was investigated for the application of Li batteries. Microstructure and morphology of the samples were studied by XRD, FTIR, FE-SEM and TEM analysis. The results showed that the H atoms of PEG are hydrogen bonded with the O atoms in V=O bonds of the V_2O_5, which effectively shielded against electrostatic interaction between the V_2O_5 interlayer and Li^+ ions. The battery of V_2O_5 nanotubes electrode showed initial specific capacity 192 $mAhg^{-1}$, whereas the PEG surfactant V_2O_5 nanotubes exhibited 204 $mAhg^{-1}$. It was found that PEG surfactant V_2O_5 nanotubes material showed high specific capacity at initial stages besides better stability was exhibited at higher cycle numbers when compared to V_2O_5 nanotubes. The cyclic performance of the PEG surfactant material seems to be improved with the role of polymeric component due to its surface reaction with V_2O_5 nanotubes during the hydrothermal synthesis.

1. Introduction

Nowadays, the contradiction between energy supplement and energy demand is becoming more and more serious in the worldwide region. Lithium-ion batteries as a green and rechargeable power source have attracted much more attention due to its extensive applications in portable electronic devices and electric vehicles [1]. It is well known that some properties such as high energy density, long cycle-life and excellent rate capability are important criteria to evaluate the electrochemical performance of lithium-ion batteries. In fact, these properties are strongly dependent on the microstructure and morphology, as well as the inherent electrochemical performance of cathode materials [2]. Therefore, extensive efforts have been devoted to exploring new synthetic methods and novel composite materials to further improve the electrochemical performance of cathode materials. Vanadium oxide nanotubes (VOx-NTs), one of the most interesting one-dimensional nanoscale electrode materials, have received considerable attention because of their special nanotubes structure and high specific surface area, which can offer many electrolyte-filled channels for faster transport of lithium-ions to the insertion sites [3–5].

However, how to prepare cathode materials with high energy density, high potential and longer cycle life is still a challenge. Vanadium oxides have interesting open-layered structures, which permit a wide variety of other molecules or cations to intercalate into the layers. In Li–ion batteries, these open-layered structures can host more Li ions to lead to higher specific capacity than commercial $LiCoO_2$ with an anion close packed lattice. Taking V_2O_5, for example, the apices of these pyramids alternate in an up–up, down–down sequence with every third row being vacant, forming a layered character for the V_2O_5 structure [6], providing the accommodating interlayer space for the intercalation reactions that are the conventional mechanism in all consumer rechargeable batteries. The intercalation of Li ion into the V_2O_5 interlayer space causes the formation of $Li_xV_2O_5$ phase, which would not change the original structural frameworks, and the intercalation process is still fully reversible, leading to the advantage of the Li–ion batteries with a high output voltage [7]. Vanadium sources are known to be abundant in the crustal rock of earth, causing the low cost, which is another advantage of vanadium oxides compared with $LiCoO_2$ with high price because of the relatively limited source of Co [8]. These advantages make vanadium oxides such as V_2O_5, VO_2, hydrated vanadium oxides, silver vanadium oxides (SVO),

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LiV_3O_8, etc. receive much attention for application in Li–ion battery.

Even though, the main disadvantage of this material is poor retention capacity during long-term cycling due to its low conductivity and poor structural stability [9]. Several approaches have been developed to solve these problems and optimize the electrochemical performance, such as modification of the crystal structure and morphology of V_2O_5 [10], doping electrochemically active additives such as TiO_2, Ag, Mo and Cu [11–13] and coating of TiO_2 on highly conductive materials [14]. The poor surface electrical conductivity of vanadium oxide can be improved by combination with conducting materials, including carbonaceous materials and conducting polymers [15].

Hydrothermal synthesis is an effective method to fabricate 1-D nanostructures because of its low temperature requirement as well as inexpensive, amenable for large scale and wide suitability for various nanomaterials. It is more effective method for the formation of nanotubes from V_2O_5 precursor in the presence of PEG polymer. Felicitous choice of a precursor is feasible to obtain desired products [16,17].

In the present paper, we synthesized V_2O_5 nanotubes and PEG surfactant V_2O_5 nanotubes by simple hydrothermal method and its structure is analyzed by XRD and FTIR studies. The dimensions of the nanotubes were determined by SEM and TEM analysis. The battery performance was estimated by the cyclic voltammograms and charge–discharge curves.

2. Experimental details

2.1. Synthesis of vanadium oxide nanotubes

In the synthesis of vanadium oxide nanotubes, 10 mmol V_2O_5 (99.5%) and 10 mmol 1-hexadecylamine ($C_{16}H_{35}N$) (Alfa Aesar Company) were poured into 20 mL distilled water and the resulting solution was stirred for 1 h, another 20 mL distilled water was added after 1 h. Then this solution was allowed to hydrolyze under vigorous stirring for 48 h at room temperature. Now this mixture solution was transferred into a Teflon-lined autoclave with a stainless steel shell and treated hydrothermally at 180 °C for 7 days. The precipitate was washed with absolute alcohol then with distilled water and allowed it at 80 °C for 5 h. In order to prepare the polymer surface reactant V_2O_5 nanotubes the above procedure was repeated with the addition of 0.1 and 0.2 mol% PEG (Aldrich, MW 20×10^3 g mol^{-1}) to the vanadium oxide-amine mixture.

2.2. Fabrication of Li batteries

The electrochemical properties were studied by CR 2025 coin-type cell with Li metal as anode electrode. The lithium cells were assembled in an argon-filled glove box at room temperature, 1 M solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate as electrolyte and pellets were made from the obtained products, acetylene black and PTFE in the ratio 6:4:1 as the positive electrode.

2.3. Measurements

The X-ray powder diffraction (XRD) measurement was performed on a PANalytical, Netherlands equipped with Cu-Kα radiation ($\lambda = 1.5418$ Å). Fourier-transform infrared absorption spectrum (FTIR) was recorded using a 60-SXB IR spectrometer with a resolution of 4 cm^{-1} in the wavelength range 400–4000 cm^{-1}. Field-emission scanning electron microscopy (FESEM) images were obtained using a JSM-6700F scanning electron microscope at 20 kV. Transmission electron microscopy (TEM) images were taken in a JEOL JEM-2100 FEF microscope operated at 200 kV. The electrochemical performance was analyzed by an Autolab Potentiostat 30 System with the scan rate of 1 mV s^{-1} at 1.5–4.0 V versus Li/Li^+ potential range and a Battery Testing System (CT-3008W 5 V/5 mA) with the constant current density of 20 mAg^{-1} at 1.5–4.0 V versus Li/Li^+ potential range.

3. Results and discussion

The X-ray diffraction patterns of V_2O_5 nanotubes, 0.1 and 0.2 mol% PEG surfactant V_2O_5 nanotubes are shown in Fig. 1. From the XRD patterns, it is clear that the V_2O_5 nanotubes and PEG surfactant nanotubes exhibited similar and low-angle reflection peaks at (001) (002) (003) (110) (210) and (310), respectively, where the structure is preserved. The peak with the highest intensity at the low diffraction angle reflects the distance between the vanadium oxide layers. The *d* value of the (001) peak is 3.53 nm and bigger than the *d* value (3.20 nm) reported by Nesper [18], which can attribute to the difference between synthesized methods. No peaks of any other phases or impurities were observed, demonstrating that V_2O_5 nanotubes with high purity could be obtained using the present synthesis process whereas the PEG worked as a surface reactant [19]. No peaks related to polymers were observed in the XRD patterns of PEG surfactant V_2O_5 nanotubes.

The FTIR spectra of V_2O_5 nanotubes and PEG surfactant V_2O_5 nanotubes were shown in Fig. 2. The strong absorption peaks appeared at 2955, 2919, 2852 and 1465 cm^{-1}, respectively, which could be assigned to the stretching and bending modes of the different C–H vibrations in the hexadecylamine template, respectively [20]. These bands are also appeared in the same wavelength region as in the PEG surfactant V_2O_5 nanotubes. Two absorption bands appeared at 3439 and 1630 cm^{-1}, could be attributed to the stretching and bending modes of O–H vibrations, respectively. This is exhibited the intercalation of water molecules into the V_2O_5 nanotubes layers [20]. Absorption bands between 400 and 1000 cm^{-1} could be indexed to various (group) vibrations of V–O type [20]. There are three major bands υ_s (V=O), υ_s (V–O–V) and υ_{as} (V–O–V) appeared at 1001, 579 and 496 cm^{-1} in V_2O_5 nanotubes and these are shifted to 997, 574 and 491 cm^{-1} in the PEG surfactant V_2O_5 nanotubes. The vibration modes (υ_s and υ_{as}) shifting exhibited oxidation and reduction states of the vanadium oxide ($V^{+4} \leftrightarrow V^{+5}$), respectively [21].

Fig. 3 shows that the scanning electron microscopy images of V_2O_5 nanotubes, PEG surfactant V_2O_5 nanotubes uniformly distributed and clearly visible. Vanadium oxide nanotubes are frequently

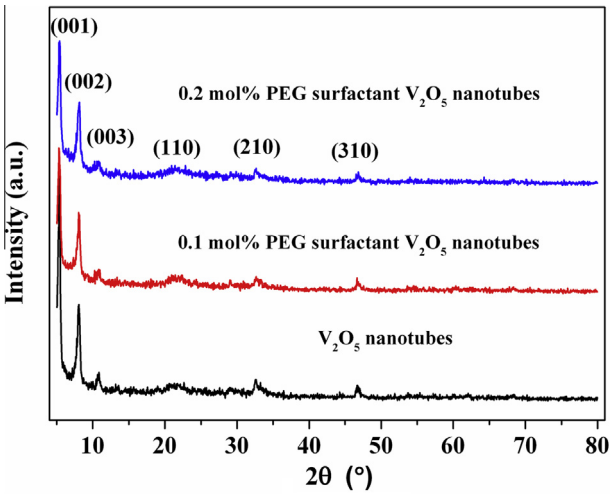

Fig. 1. X-ray diffraction patterns of V_2O_5 nanotubes and PEG surfactant V_2O_5 nanotubes.