Materials Research Bulletin 49 (2014) 291–296

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

One-step synthesis of dense and spherical nanostructured V_2O_5 particles for cathode of lithium batteries and their electrochemical properties

Shan Lin, Bin Shao, Izumi Taniguchi *

Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, 12-1, Ookayama-2, Meguro-ku, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 22 August 2013
Accepted 30 August 2013
Available online 8 September 2013

Keywords:
A. Ceramics
B. Microstructure
C. Electrochemical measurements
D. Electrochemical properties
D. Energy storage

ABSTRACT

A one-step synthesis of V_2O_5 was directly achieved via ultrasonic spray pyrolysis at various synthesis temperatures ranging from 500 to 700 °C. The V_2O_5 prepared at 500 °C is dense and spherical nanostructured particles, which consist of primary particles with a size of approximately 100 nm. The morphology change remarkably progresses with increasing synthesis temperatures from 500 to 700 °C. The electrochemical performance of a cathode comprising dense and spherical nanostructured V_2O_5 particles prepared at 500 °C was investigated by galvanostatic discharge–charge cycling and cyclic voltammetry. From the discharge–charge cycling, the initial discharge capacity of the cathode was found to be about 403 mAh g^{-1} in the potential range of 1.5–4.0 V, but it decreased owing to inherent phase changes with repeated cycling. The potential range significantly affects the cycle performance, and the V_2O_5 cathode showed good cycle performance in the potential range of 2.5–4.0 V.

1. Introduction

Since the commercialization of lithium ion batteries in the early 1990s, the increasing demand for high power density, high energy efficiency, and good rate performance in lithium ion batteries has prompted extensive investigation of alternative cathode materials. Vanadium pentoxide or vanadia (V_2O_5) was identified as one of the useful cathode materials for lithium ion batteries owing to its unique isotropic structure, high energy density, low cost, and abundant source [1,2]. The electrochemical reduction of V_2O_5 can occur in a large potential window between 4.0 and 1.5 V vs. Li/Li^+, where approximately three moles of lithium per mole of V_2O_5 could be theoretically inserted, leading to a specific charge of approximately 440 mAh g^{-1} [3–5]. However, the rapid decrease in its capacity and the low practical capacity of crystalline V_2O_5 limit its wider application [4–6]. To achieve better electrochemical performance, various morphological V_2O_5 cathode materials have been synthesized. In these cathodes, nanostructured V_2O_5 particles are quite an attractive material because of its small primary particle size, which reduces the diffusion distance for Li ions, its large surface area, and its ability to undergo simultaneous phase transformation, resulting in better reversibility and cyclability [7–13].

Recently, Feng et al. [5] have reported that spherical and hollow V_2O_5 particles can be synthesized from a starting solution, consisting of V_2O_5, $H_2C_2O_4$, and citric acid dissolved in distilled water by a spray pyrolysis method followed by heat-treatment in the temperature range from 350 to 600 °C for 6 h. Wang et al. [14] also investigated the synthesis of V_2O_5/C composites from V_2O_5, HNO_3 and citric acid precursors by spray pyrolysis. The as-prepared V_2O_5/C particles were hollow in shape and contained amorphous carbon with low electronic conductivity owing to the low synthesis temperature of 500 °C [15]. The hollow V_2O_5 particles were not suitable as a cathode material of lithium batteries owing to their low packing density and weak electrode strength [16,17]. Moreover, the use of V_2O_5/C composites with low conductivity carbon make it difficult to improve the rate capability of cells.

Thus far, we have reported that dense and spherical nanostructured $LiMn_2O_4$ particles [18] and their substituted forms [18–20] and dense and spherical nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles [21] can be successfully prepared by ultrasonic spray pyrolysis, and that they exhibit excellent electrochemical performance when used as active electrode materials for lithium ion batteries. In this study, we investigate the one-step synthesis of

* Corresponding author. Tel.: +81 3 5734 2155; fax: +81 3 5734 2155.
E-mail addresses: taniguchi.i.aa@m.titech.ac.jp, itaniguc@chemeng.titech.ac.jp (I. Taniguchi).

0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.08.071

dense and spherical nanostructured V_2O_5 particles from an ammonium metavanadate precursor dissolved in distilled water by ultrasonic spray pyrolysis and their application as electrodes in lithium batteries.

2. Experimental

The precursor solution was prepared by dissolving ammonium metavanadate (NH_4VO_3, 98% purity) in distilled water with heating to obtain a concentration of 0.068 mol dm^{-3}. V_2O_5 was prepared by ultrasonic spray pyrolysis at synthesis temperatures from 500 to 700°C. A schematic diagram of the experimental apparatus used has been provided elsewhere [22]. It consists of an ultrasonic nebulizer (1.7 MHz, Omron Co., Ltd., Model NE-U12), a laminar flow aerosol reactor (a high-quality ceramic tube of 20 mm inner diameter and 1.50 m length) and an electrostatic precipitator. The precursor solution was atomized at a frequency of 1.75 MHz using the ultrasonic nebulizer. The generated droplets were carried to the reactor by air at a flow rate of 1 dm^3 min^{-1}. If we assume a plug flow in the reactor, the residence time of the particles is 21 s. The particles obtained from the reactor exit were collected using the electrostatic precipitator, which was operated at 180 °C, to prevent the condensation of vapor on the particles.

The crystalline phases of the samples were identified by X-ray diffraction (XRD, Rigaku, Ultima IV with D/teX Ultra) analysis using Cu-Kα radiation. The lattice parameters of the materials were refined by Rietveld analysis using the integrated X-ray powder diffraction software package PDXL (Rigaku, Version 1.3.0.0). The surface morphology and interior structure of samples were examined by field-emission scanning electron microscopy (FE-SEM, Hitachi, S4500). The samples for the interior structure observation were prepared at 5 kV using a cross section polisher (JEOL, CP-mk2)

Electrochemical characterization was performed by assembling a CR2032 coin cell under a galvanostatic charge–discharge condition. The cell comprised a lithium metal negative electrode and V_2O_5 positive electrodes, which were separated by a microporous polypropylene separator. 1 mol dm^{-3} $LiPF_6$ solution in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1 volume ratio (Tomiyama Pure Chemical Co., Ltd.) was used as the electrolyte. The V_2O_5 electrode consisted of 70 wt.% V_2O_5, 10 wt.% polyvinylidene fluoride (PVdF) as a binder and 20 wt.% acetylene black as a conductor. The cycling performance of the cells was studied galvanostatically in various potential ranges using multichannel battery testers (Hokuto Denko, HJ1010mSM8A). The discharge–charge rate was 0.1 C (1 C = 442 mA g^{-1}).

Cyclic voltammetry (CV) was conducted over a potential range from 2.5 to 4.0 V at a scanning rate of 0.1 mV s^{-1} using a Solartron SI 1287 electrochemical interface. All the electrochemical measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared by ultrasonic spray pyrolysis at synthesis temperatures from 500 to 700 °C. The JCPDS card patterns of V_2O_5 are also shown in the figure. The diffraction peaks of all the samples are identified as those of the orthorhombic V_2O_5 structure with the space group *Pmmn* without any impurity peaks. The refined lattice parameters for the samples prepared at synthesis temperatures from 500 to 700 °C were in a good agreement with those of standard orthorhombic V_2O_5 (JCPDS 41-1426; a = 11.5160 Å, b = 3.5656 Å and c = 4.3727 Å), as shown in Table 1.

The surface morphology of the V_2O_5 particles is shown in Fig. 2. The V_2O_5 sample prepared at 500 °C is dense and spherical

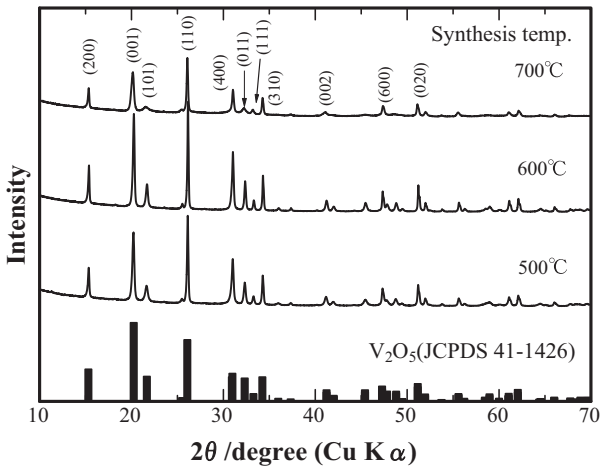

Fig. 1. XRD patterns of the samples synthesized at different temperatures from 500 to 700 °C by ultrasonic spray pyrolysis.

nanostructured particles, which consist of primary particles with a size of approximately 100 nm. The morphology change markedly progresses with increasing synthesis temperatures from 500 to 700 °C. The primary particle growth of V_2O_5 progresses at synthesis temperatures from 500 to 600 °C. On the other hand, the marked morphology change from dense and spherical nanostructured particles to spherical densified particles takes place at synthesis temperatures from 600 to 700 °C, which may be due to the low melting point of V_2O_5 (690 °C).

Fig. 3 shows the interior structure of the V_2O_5 particles. It can be clearly seen from the SEM images that the V_2O_5 particles prepared by ultrasonic spray pyrolysis are dense and spherical nanostructured particles. Moreover, we can confirm from Figs. 2 and 3 that the dense and spherical nanostructured V_2O_5 particles can be successfully prepared at 500 °C by the present method. To the best of our knowledge, such V_2O_5 particles have not been previously reported.

The electrochemical properties of V_2O_5 prepared by ultrasonic spray pyrolysis were also systemically investigated at a discharge–charge rate of 0.1 C. Fig. 4 shows the initial discharge profiles of the V_2O_5 samples prepared at synthesis temperatures of 500, 600 and 700 °C, which exhibit discharge capacities of 403, 397, and 351 mAh g^{-1}, corresponding to the intercalation of approximately 2.74, 2.69, and 2.38 mol of Li^+ into 1 mol of V_2O_5, respectively. These values may indicate the formation of ω-$Li_xV_2O_5$ ($x > 2$). Sun et al. [23] reported that the theoretical discharge capacity of 274 mAh g^{-1} for $Li_2V_2O_5$ is rarely reached by crystalline V_2O_5. However, these results clearly show that higher initial discharge capacities are obtained by the dense and spherical nanostructured V_2O_5 particles prepared by the ultrasonic spray pyrolysis. Furthermore, there are four potential plateaus in the discharge curve for each sample that originate from phase transitions between α-V_2O_5, ε-$Li_xV_2O_5$ ($0.35 < x < 0.7$), δ-$Li_xV_2O_5$ ($x = 1$), γ-$Li_xV_2O_5$ ($1 < x \leq 2$), and ω-$Li_xV_2O_5$ ($x > 2$), respectively.

Table 1
Lattice parameters of V_2O_5 prepared by ultrasonic spray pyrolysis at different temperatures from 500 to 700 °C.

Synthesis temperature [°C]	Lattice parameters		
	a [Å]	b [Å]	c [Å]
500	11.4976	3.5630	4.3801
600	11.5034	3.5629	4.3788
700	11.4998	3.5709	4.3886
V_2O_5 (JCPDS 41-1426)	11.5160	3.5656	4.3727