



Correlation between porous structure and electrochemical properties of porous nanostructured vanadium pentoxide synthesized by novel spray pyrolysis



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HIGHLIGHTS

- Porous nanostructured V_2O_5 was prepared by novel spray pyrolysis.
- NH_4NO_3 additive in precursor solution enables to morphology control of V_2O_5 .
- Unique porous V_2O_5 could be obtained by tuning concentration of NH_4NO_3 .
- Correlation between porous structure and electrochemical properties were studied.
- The porous nanostructured V_2O_5 electrode delivered a 180 mAh g^{-1} at 1200 mA g^{-1} .

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ABSTRACT

Porous nanostructured vanadium pentoxide (V_2O_5) particles were successfully prepared by spray pyrolysis (SP) in a precursor solution with an ammonium nitrate (NH_4NO_3) additive. The correlation between the porous structure and the electrochemical properties of the V_2O_5 particles was investigated. The porous structure markedly changed upon increasing the concentration of NH_4NO_3 in the precursor solution from 0 to 0.408 mol L^{-1} . Pore structure analysis based on N_2 adsorption-desorption isotherm measurements indicated that porous nanostructured V_2O_5 particles with a pore size of less than 100 nm can be prepared by the novel SP method and that an increase in the NH_4NO_3 concentration in the precursor solution can enlarge the pores in the V_2O_5 particles, especially those with a size between 20 and 80 nm. The porous nanostructured V_2O_5 prepared with an NH_4NO_3 concentration of 0.272 mol L^{-1} exhibited a first discharge capacity of 400 mAh g^{-1} at 20 mA g^{-1} . The unique porous structure of V_2O_5 particles significantly enhanced the rate performance and exhibited a first discharge capacity of 180 mAh g^{-1} at 1200 mA g^{-1} , which is much higher than that of dense V_2O_5 particles (70 mAh g^{-1}).

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1. Introduction

Electrical energy storage is expected to be a critical component of the world's future energy system, performing load-leveling operations to increase the penetration of renewable and distributed generation [1]. Among the many available energy storage technologies, lithium-ion batteries have the features of high energy density, high power density, long life and low environmental impact compared with conventional rechargeable batteries, such as

lead-acid, nickel-cadmium and nickel-metal hydride batteries. As a result, they have rapidly become widespread as a power supply for portable devices [2].

However, the energy density of lithium-ion batteries is typically limited by the ability of electrons to insert/de-insert in the cathode materials. Theoretically, the use of multi-electron redox materials is an effective means of developing a new rechargeable battery with higher energy density [3]. Among the potential multi-electron redox materials, vanadium pentoxide (V_2O_5) is attracting great attention as a promising cathode material owing to its low cost, relatively low toxicity, high safety and the potential to insert three electrons, giving a theoretical capacity of 440 mAh g^{-1} [4,5]. However, its moderate electrical conductivity and the poor

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diffusion coefficient of lithium ions [6,7] greatly limit its practical application.

Porous structured materials are becoming one of the most powerful means of improving the electrochemical performance of electrode materials [8] as they involve the combination of both a void space and nanoscale particles. As a result, the contact area between the electrolyte and electrode can be increased and the diffusion distance of lithium ions in the electrode can be reduced [9]. Thus far, the preparation of materials with porous structure has been performed by various methods such as the sol-gel process [10–12], electrospinning [13] and hydrothermal synthesis [14]. However, most of these methods are either complicated or employ expensive agents. The spray pyrolysis (SP) method has several advantages such as a low cost, continuous operation, short processing time and homogeneous chemical composition of the prepared materials [15,16]. In our previous studies, several cathode materials for lithium-ion batteries, such as $\text{Li}_2\text{FeSiO}_4$ [17], LiCoPO_4 [18], LiMnPO_4 [19], LiMn_2O_4 [20,21], LiFePO_4 [22] and $\text{Li}_2\text{FeP}_2\text{O}_7$ [23] were prepared by SP and then their electrochemical properties were investigated. In this study, we have developed a novel SP route for preparing V_2O_5 with various porous structures, and we investigated the correlation between the porous structure and the electrochemical properties.

2. Experimental

2.1. Preparation of porous nanostructured V_2O_5 particles

The precursor solution was prepared by dissolving the required amounts of ammonium metavanadate (NH_4VO_3) and ammonium nitrate (NH_4NO_3) in distilled water. The concentration of NH_4VO_3 was fixed at 0.068 mol L^{-1} and the concentration of NH_4NO_3 was varied from 0 to 0.408 mol L^{-1} . All chemicals were purchased from Wako Pure Chemical Industries Ltd., Japan.

A schematic diagram of the experimental apparatus that we developed has been provided elsewhere [17]. It mainly consists of an ultrasonic nebulizer (1.7 MHz, Omron Co., Ltd., Model NE-U17), a laminar flow aerosol reactor (a high-quality ceramic tube of 70 mm inner diameter and 1.5 m length) and an electrostatic precipitator. The precursor solution was atomized at a frequency of 1.7 MHz using the ultrasonic nebulizer. The generated droplets were carried to the reactor by air at a flow rate of 3 L min^{-1} and the reactor temperature varied from 400 to 700 °C. The particles obtained from the reactor exit were collected using the electrostatic precipitator, which was operated at 150 °C to prevent the condensation of vapor on the particles.

2.2. Physical characterization

The crystalline phases of samples were identified by X-ray diffraction (XRD, Rigaku, Ultima IV with D/teX Ultra) analysis with Cu-K α 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 the samples were examined by field-emission scanning electron microscopy (FE-SEM, Hitachi, S4500). The samples used for the observation of the interior structure were prepared at 5 kV using a cross-section polisher (JEOL, CP-mk2). Nitrogen (N_2) adsorption-desorption measurements were performed at a liquid N_2 temperature of 77 K using a Micromeritics TriStar II 3020 system. Before the measurements, a 0.5 g sample was outgassed under vacuum for 5 h at 300 °C. Pore size distributions were estimated from the desorption branches of the isotherms by the Barrett-Joyner-Halenda (BJH) model, and the Brunauer-Emmett-Teller (BET)

specific surface area was determined from the N_2 adsorption-desorption isotherms of the samples.

2.3. Electrochemical characterization

The electrochemical performance of the porous nanostructured V_2O_5 particles was investigated using a CR2032 coin-type cell. The cell comprised a lithium metal negative electrode and a positive electrode, which were separated by a microporous polypropylene film. 1.0 mol dm^{-3} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a 1:1 vol ratio (Tomiya Pure Chemical Co., Ltd.) was used as the electrolyte. The positive electrode consisted of 80 wt% V_2O_5 , 10 wt% polyvinylidene fluoride (PVdF) as a binder and 10 wt% acetylene black. A slurry prepared by dispersing these materials in 1-methyl-2-pyrrolidinone (NMP) was spread uniformly onto an aluminum foil using the doctor blade technique. After drying the slurry-coated foil in a vacuum oven for 4 h at 100 °C, it was punched into circular discs, which were then scraped to standardize their area to 1 cm^2 . The loading of the electrode was approximately 2.0 mg cm^{-2} . All cells were assembled inside a high-purity argon-filled glove box (99.9995% gas purity). The cells were galvanostatically cycled between 1.5 and 4 V at different current densities from 20 to 1200 mA g^{-1} on multichannel battery testers (Hokuto Denko, HJ1010mSM8A). The current density and specific capacity were calculated from the mass of V_2O_5 in the electrode.

Cyclic voltammetry (CV) measurements were performed in a potential window of 1.5–4.0 V (vs Li/Li^+) at a scanning rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron 1255B frequency response analyzer connected to a Solartron SI 1287 electrochemical interface. The amplitude of the ac signal was 10 mV in the frequency range from 100 kHz to 0.01 Hz. The electrochemical measurements were performed at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of V_2O_5 particles

Fig. S1 shows the XRD patterns of the samples prepared by SP at synthesis temperatures from 400 to 700 °C. The diffraction peaks of all samples can be indexed to the orthorhombic V_2O_5 structure with the space group *Pmmn* (ICSD card no. 60767) [24], while the sample prepared at 400 °C includes impurities, which may result from the incomplete decomposition and crystallization of vanadium salts at the low temperature.

The morphology of the samples prepared by SP at synthesis temperatures from 400 to 700 °C was characterized by FE-SEM analysis, as shown in Fig. S2a. The V_2O_5 particles obtained by SP at 400 and 500 °C are spherical in shape. An increase in the synthesis temperature from 500 to 600 °C leads to the particle morphology changing from spherical particles to nanorod aggregates owing to grain growth. However, the V_2O_5 particles prepared at 700 °C are also spherical in shape. It may be concluded from the melting point of V_2O_5 (690 °C) and the variation of the specific surface area, as shown in Fig. S2b, that spherical densified V_2O_5 (named Dense- V_2O_5) particles are synthesized at 700 °C by SP.

Fig. S3 shows the first charge-discharge profiles of the V_2O_5 samples prepared at synthesis temperatures from 400 to 700 °C. The V_2O_5 sample prepared at 500 °C, which has the highest specific surface area, exhibits the largest discharge capacity (347 mAh g^{-1}). Thus, the synthesis temperature was fixed at 500 °C and then further investigation was carried out on V_2O_5 samples prepared by the novel SP method, i.e., SP with an NH_4NO_3 additive in the precursor solution.

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