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Thermally Controlled V_2O_5 Nanoparticles as Cathode Materials for Lithium-Ion Batteries with Enhanced Rate Capability

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ABSTRACT

Vanadium pentoxide (V_2O_5) is an attractive cathode material for lithium-ion batteries (LIBs) because of its low cost, high abundance, and relatively high theoretical capacity (294 mA h g^{-1} with two lithium insertions/extractions per unit formula at 2.0–4.0 V). However, practical applications of V_2O_5 are hampered by its poor structural stability, low electrical conductivity, and slow ion diffusion kinetics, resulting in poor long-term cycling stability and rate performance. In this study, V_2O_5 nanoparticles are synthesized by a fast sol-gel method with citric acid ($C_6H_8O_7$) at 400, 500, 600, and 700 °C. The thickness of the amorphous layers on the surface of the V_2O_5 nanoparticles is controlled from approximately 4–5 to 1–2 nm by adjusting the calcination temperature. The V_2O_5 nanoparticles synthesized at 600 °C show better electrochemical performances than the other samples. They exhibit a high initial discharge capacity of 276 mA h g^{-1} between 2.1 and 4.0 V at a rate of 1 C, and good capacity retention of 83% after 50 cycles. Even at 10 C rate, a discharge capacity of about 168 mA h g^{-1} is obtained after 100 cycles. The excellent rate capability and cycling stability are also achieved at current densities of 0.5–20 C.

1. Introduction

Over the last couple of decades, lithium-ion batteries (LIBs) have become one of the most effective energy-storage systems because of their high energy densities, high operating voltages, environment friendliness, and long cycling lifetimes [1–3]. Recently, there have been many attempts to use LIBs as the power source for electric and hybrid electric vehicles, which has motivated the development of high-performance cathode materials with good cycling stability, reversible capacities, and rate capabilities [4,5]. Significant improvements have been achieved in the cycling stabilities and rate capabilities of conventional cathode materials such as $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $LiMn_2O_4$, and $LiFePO_4$. However, the specific reversible capacities have been restricted by the intrinsic redox chemistry, since there is only one lithium insertion/extraction per formula unit [6–8].

Vanadium pentoxide (V_2O_5) is a promising cathode material because of its high energy density, high abundance, and low cost [9–11]. The high theoretical capacities of V_2O_5 are especially attractive; for example, 294 mA h g^{-1} at 2.0–4.0 V. However, its low intrinsic electrical conductivity (10^{-2}–10^{-3} S cm^{-1}) and sluggish lithium-ion diffusion kinetics ($\sim 10^{-12}$ cm^2 s^{-1}) cause poor capacity retention and rate capabilities [12–15]. Furthermore, repeated phase transformations of $Li_xV_2O_5$ during charge/discharge processes (e.g., α phase for $x < 0.1$, ε phase for $0.35 < x < 0.7$, δ phase for $x = 1$, γ phase for $1 < x < 3$, and ω phase for $x = 3$) often cause structural instabilities, thus degrading the cycling performance [16–18]. These drawbacks have hindered the practical applications of V_2O_5 in commercial LIBs. To solve these problems, numerous investigations have been conducted into the fabrication of porous materials, nanostructures, and nanocomposites with conductive additives [5,10–12,14,17,19–42]. In particular, V_2O_5/carbon composite materials (for example, V_2O_5/carbon tube-in-tube, V_2O_5/reduced graphene oxide (r-GO), and carbon-coated V_2O_5) show significantly improved electrochemical performance over bare V_2O_5 [11,16,32,39,43,44]. However, impregnation of V_2O_5 into carbon materials often requires excess carbon in the electrode composites to increase their electrical conductivity at the expense of the filling density of active substance in the electrode [11,32]. Several studies have reported surface modification of V_2O_5 with thin, conductive carbon layers by using ordered mesoporous carbon (OMC) as a carbon source [39] or vanadium alkoxides as vanadium and carbon sources [16,43]. However, there have been few reports to control the thickness of amorphous layers on the surface of V_2O_5 particles and to investigate their influence on the electrochemical performances as cathode materials in LIBs.

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In this paper, we report a facile and scalable method for the synthesis of V_2O_5 nanoparticles with various thickness of amorphous layers through a sol–gel method and controlled calcination at 400, 500, 600, and 700 °C. Citric acid ($C_6H_8O_7$) was used as a chelating/reducing agent for preparing V_2O_5 nanoparticles. The electrochemical performances of these four samples were thoroughly compared to identify the optimal synthetic conditions for the V_2O_5 cathode materials.

2. Experimental

2.1. Sample Preparation

V_2O_5 nanoparticles were synthesized by a fast sol–gel method using NH_4VO_3 and citric acid. Citric acid (≥99.5%, Aldrich; 4.03 g) was first dissolved in distilled water (10 mL) at 60 °C under stirring, and then NH_4VO_3 (≥99.0%, Aldrich; 2.46 g) was carefully added to the solution. The color of the solution changed from yellow (V^{5+}) to blue (V^{4+}), indicating that citric acid reduced V^{5+} ions of NH_4VO_3 to V^{4+} ions through the formation of a soluble intermediate product $(NH_4)(VO)(C_6H_5O_7)$ [45]. The molar ratio of NH_4VO_3 and citric acid was adjusted to 1:1. The mixture was heated at 80 °C under continuous stirring until the excess water had evaporated, giving a dark-blue gel. The gel precursor was heated in an oven at 80 °C for 12 h to form a dry blue powder. The powder sample was calcined at 400–700 °C for 6 h at a heating rate of 10 °C min^{-1} in air to yield crystalline V_2O_5 nanoparticles. Four different samples were prepared separately at 400, 500, 600, and 700 °C and were designated C400, C500, C600, and C700, respectively. Bare V_2O_5 was prepared for the comparison in the same synthetic conditions as those of C400 but, oxalic acid (98%, Aldrich; 3.78 g) was used in the place of citric acid [12,44].

2.2. Characterization

X-ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FT-IR), Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Field-Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy, and Elemental Analysis (EA).

The XRD patterns of the samples were obtained using a Rigaku Ultima IV D/MAX X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å). The surface chemical composition and chemical states of vanadium of the samples were investigated by XPS measurements using a MultiLab 2000 spectrometer (Thermo VG Scientific, UK) with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). The binding energies were calibrated with reference to C1s at 284.6 eV. The obtained XPS spectra were characterized with XPSPeak 4.1 software. FT-IR spectroscopy was carried out on KBr pellets using a Nicolet 380 FT-IR spectrometer (Thermo Scientific) in the range 400–4000 cm^{-1}. TGA/DTA measurements were performed on TG-DTA 2020 (Bruker) in the temperature range of 25 to 850 °C with a heating rate of 10 °C/min in air. The morphology of the samples was characterized by FESEM (JEOL JSM-6700F), and the nanostructure was investigated using TEM (JEOL JEM-2010) microscopes. The carbon contents of the samples were estimated using an element analyzer (Flash EA 1112). Raman spectra were measured on Alpha 300R (WITec) using a He–Ne laser with 633 nm in wavelength.

2.3. Electrochemical Measurements

The cathode electrodes were prepared by mixing 70 wt% active material, 20 wt% carbon black (Super P Li carbon, Timcal) as a conductive additive, and 10 wt% poly(vinyl difluoride) (PVdF) as a binder in N-methylpyrrolidone (Aldrich) using a mortar. The resulting slurry was applied to an aluminum foil using a doctor blade and dried at 80 °C for 1 h. After this predrying, the electrodes were roll-pressed in order to reduce their thickness from ~60 to ~20 μm and dried in a vacuum oven at 110 °C for 12 h. The electrodes were punched into 14-mm-diameter disks. The cathode loading was about 1.8 mg/cm^2. Coin cells were assembled in an argon-filled glove-box. Lithium metal and a Celgard 2400 polypropylene membrane were used as the counter electrode and separator, respectively. The electrolyte used was 1.0 M $LiPF_6$ in an ethylene carbonate/dimethyl carbonate mixture (1:1 v/v) (Ukseung Ltd.). Galvanostatic charge/discharge experiments were carried out at different current densities in the voltage range 4.0–2.1 V using a WonATech WBCS3000 battery-testing system. (Here, 1C refers to two lithium ions per formula unit of V_2O_5 discharged/charged in 1 h.) The cells were discharged using constant-current mode to 2.1 V and then charged in constant-current/constant-voltage mode to 4.0 V. After the cells had been charged to 4.0 V, an additional voltage-holding step was performed at 4.0 V, with a 10% cutoff of the original current value. The specific capacities of the samples were calculated on the basis of the total mass of electrode materials. Cyclic voltammetry (CV) was performed using a WonATech WBCS3000 battery-testing system at a scan rate of 1 mV s^{-1} over the voltage range 4.0–2.1 V. Electrochemical impedance spectra (EIS) were obtained using WonATech ZIVE SP2 at a charged potential of 4.0 V after the second cycle in the frequency range 10^{-2}–10^{5} Hz; the AC signal amplitude was 10 mV. All tests were conducted at 25 °C. The Nyquist plots (Z″ vs. Z′) were analyzed with ZMAN (Version 2.2 f3, WonATech Co., Ltd).

3. Results and Discussion

3.1. Structural and Morphological Characterization

Fig. 1 shows the XRD patterns of the synthesized V_2O_5 samples. All the peaks were consistent with orthorhombic V_2O_5 (JCPDS file 41-1426, space group Pmnm) without any impurity peaks [11,18,39]. The average grain sizes of C400, C500, C600, and C700 were calculated to be 37.9, 41.5, 61.9, and 61.1 nm, respectively, from the (2 0 0), (0 0 1), (1 1 0), and (4 0 0) peaks using the Debye–Scherrer equation. This shows that the sample crystallinity increased with the calcination temperature. However, C700 shows similar crystallinity to that of C600, probably due to the formation of structural defects induced by the melting of V_2O_5 at about 690 °C [39] and the reduction of V^{5+} to V^{4+} by the residual carbon moieties around it at the high temperature. No obvious diffraction peak related to residual carbon was found, indicating

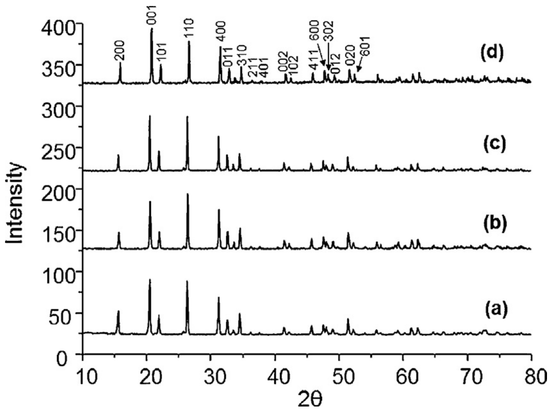

Fig. 1. XRD patterns of (a) C400, (b) C500, (c) C600, and (d) C700.