Journal of Industrial and Engineering Chemistry 52 (2017) 314–320

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

The studies of lattice parameter and electrochemical behavior for $Li_3V_2(PO_4)_3$/C cathode materials

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ARTICLE INFO

Article history:
Received 2 January 2017
Received in revised form 31 March 2017
Accepted 1 April 2017
Available online 9 April 2017

Keywords:
Lithium-ion battery
Cathode
Lithium vanadium phosphate
Lattice parameter
Carbon coating

ABSTRACT

Single-phase, nano-sized $Li_3V_2(PO_4)_3$/C materials with the monoclinic structure were prepared by a modified sol–gel method, in which the precursor materials were sintered at 750, 800, 850, and 900 °C, respectively The X-ray diffraction (XRD) patterns of all the materials were consistent with the monoclinic structure without any impurities. The LVP/C composite sintered at 800 °C was selected as the most promising material on the basis of the lattice parameters ($a = 8.605$ Å, $b = 8.596$ Å, $c = 14.732$ Å, $\beta = 125.20°$, $V = 890.59$ Å^3), crystallite size (99 nm), and morphology (5–6 nm carbon layer). The LVP/C composite sintered at 800 °C showed a high specific capacity with excellent kinetic properties (capacity of 130 and 170 mAh g^{-1} at voltages of 3.0–4.3 and 4.8 V at 0.1C, 25 °C), which showed about 98%, 86% of its theoretical capacity, respectively.

Introduction

Olivine-structured $Li_3V_2(PO_4)_3$ (LVP) has attracted much attention as a potential cathode material in Li-ion batteries for electric vehicle (EV) applications because of the excellent safety features derived from the strong covalent P—O bond. Moreover, LVP has higher energy density than $LiFePO_4$ due to the higher redox potentials of V^{3+}/V^{4+} (3.6–4.1 V) and V^{4+}/V^{5+} (4.6 V) compared to Fe^{3+}/Fe^{2+} (3.4 V) [1]. LVP has a theoretical capacity of 197 mAh g^{-1} at 3.0–4.8 V, which is the highest among the capacities of all phosphate cathode materials [2]. However, the electrical conductivity of LVP is extremely low, about 10^{-8} S cm^{-1} at room temperature, leading to poor electrochemical kinetic characteristics [3]. Therefore, extensive research has been conducted to improve the electronic conductivity of LVP materials. Such approaches include particle size reduction, cation doping, and carbon coating; it is well known that carbon coating is the most effective way to enhance the electronic conductivity of LVP [4,5]. Methods such as solid-state reaction, microwave irradiation, sol-gel methods, and hydrothermal processes have been used to synthesize LVP/C materials [6–9]. It is reported that reduction of the particle size to nanometer dimensions can be achieved with the sol–gel process, thus reducing the sintering temperature and time [10]. However, little is known about the electrochemical behavior of LVP/C materials as the lattice parameters of the LVP/C material is changed [11–13].

In the present study, we investigate the electrochemical properties of nano-crystalline LVP/C materials prepared via the sol–gel process, where the effect of the sintering temperature is investigated. The crystal structure, crystallite size, and morphology of the synthesized LVP/C composites are studied via X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrochemical cells are evaluated based on charge-discharge, cyclic voltammetry, and impedance spectroscopy analyses.

Experimental

The nano-crystalline LVP/C materials were synthesized via a sol–gel process. Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$: Samchun Chemicals, 98%), vanadium pentaoxide (V_2O_5: Samchun Chemicals, 99%), ammonium phosphate monobasic ($NH_4H_2PO_4$: JUNSEI, 99%), and oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$: Samchun Chemicals, 99%) were used as starting materials. Fig. 1 shows the schematic of the sol–gel technique for synthesis of the LVP/C materials. Initially, vanadium pentaoxide and oxalic acid dihydrate

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http://dx.doi.org/10.1016/j.jiec.2017.04.004
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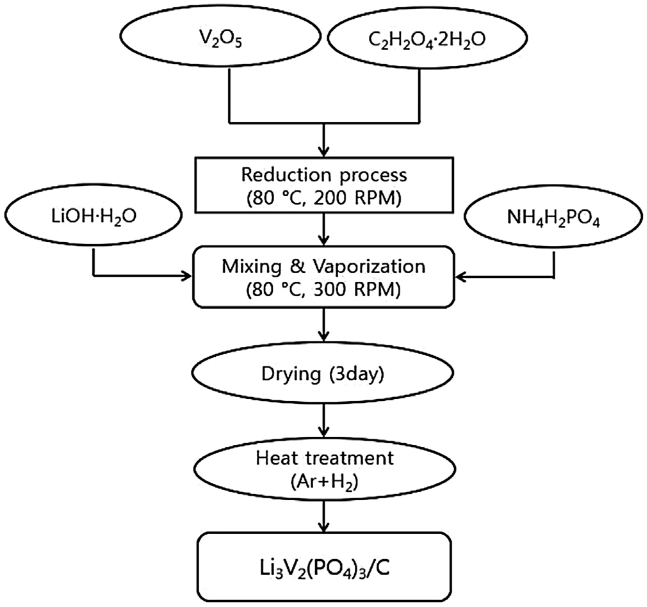

Fig. 1. Schematic diagram of sol–gel synthesis for LVP/C materials.

(in a stoichiometric mole ratio of 1:3) were dissolved in deionized water with stirring at 200 rpm at 80 °C until the reduction of V^{5+} was complete, where oxalic acid dihydrate was used as a chelating agent (reducing agent) and carbon source. Subsequently, solutions of lithium hydroxide monohydrate and ammonium phosphate monobasic in a stoichiometric mole ratio of 1:1 were also blended with the aforementioned mixture with continuous stirring at 300 rpm at 80 °C until the end of the gel reaction. The wet-gel was dried at 110 °C in a drying oven for one day and in a vacuum oven for two days. The dry-gel, as a precursor, was pre-calcined at 400 °C for 5 h under a gas mixture comprising 95% Ar and 5% H_2. The dry-gel precursor was ground for 30 min and then pressed into pellets at 60 MPa and subsequently sintered in the range of 750 to 900 °C for 10 h under a gas flow of 95% Ar and 5% H_2. The LVP/C materials were pulverized again for 30 min and sieved to obtain fine powders with a diameter of less than 45 μm.

The crystal structures of the LVP/C materials were studied using XRD (XPert Pro, PANalytical, Netherlands) by employing Cu-Kα radiation (λ = 1.5406 Å). The lattice parameters and crystallite size were estimated by the Rietveld refinement method. The morphology of the LVP/C materials was observed using field emission scanning electron microscopy (FESEM; HITACHI S-4700, Japan) and TEM (JEM 2200FS, Jeol, Japan).

Electrochemical evaluation of the LVP/C materials was conducted by using three-electrode cell and 2032 coin cell. The cathode slurry was prepared by blending 80 wt% LVP/C material with 10 wt% Super-P carbon black and 10 wt% poly(vinylidene) fluoride (PvdF) in *N*-methyl-2-pyrrolidone (NMP). The slurry was coated onto aluminum foil and then dried at 110 °C for 24 h; the thickness of the cathode was controlled by a roll-pressor. The cathode was re-dried under vacuum for 4 h at 80 °C. Lithium metal was used as the anode, 1 M $LiPF_6$ in ethylene carbonate–diethyl carbonate (EC–DEC) (1:1 in volume) was used as the electrolyte, and Celgard 2400 as the separator.

All parts of the cell were assembled in a dry room, and the electrochemical evaluations were conducted at room temperature. Galvanostatic charge-discharge analysis was performed on a WBCS3000S (Wonatech) instrument at 3.0–4.3 V and 3.0–4.8 V. Cyclic voltammograms were also acquired using an SP-150 (BioLogic) instrument with three-electrode cell at scan rate of 0.2 mV s^{-1}, where Li-metal was used as the reference and counter electrodes. Electrochemical impedance spectroscopy (EIS) measurement was conducted in the frequency range of 1 MHz to 100 m Hz with a signal amplitude of 5 mV.

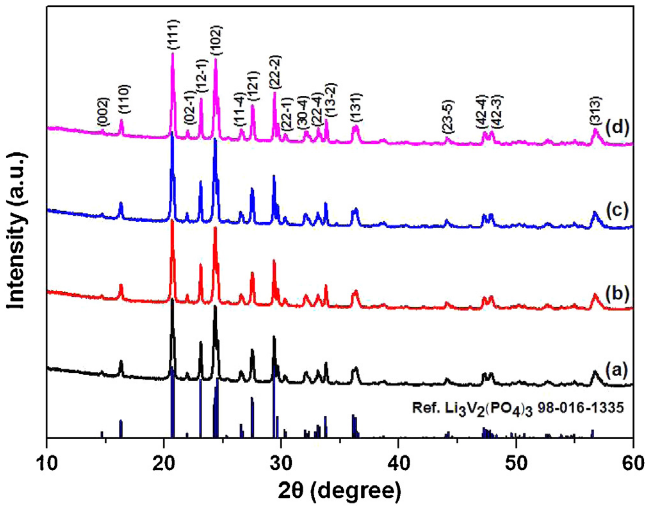

Fig. 2. XRD patterns of LVP/C materials sintered at 750 °C (a), 800 °C (b), 850 °C (c), and 900 °C (d) for 10 h.

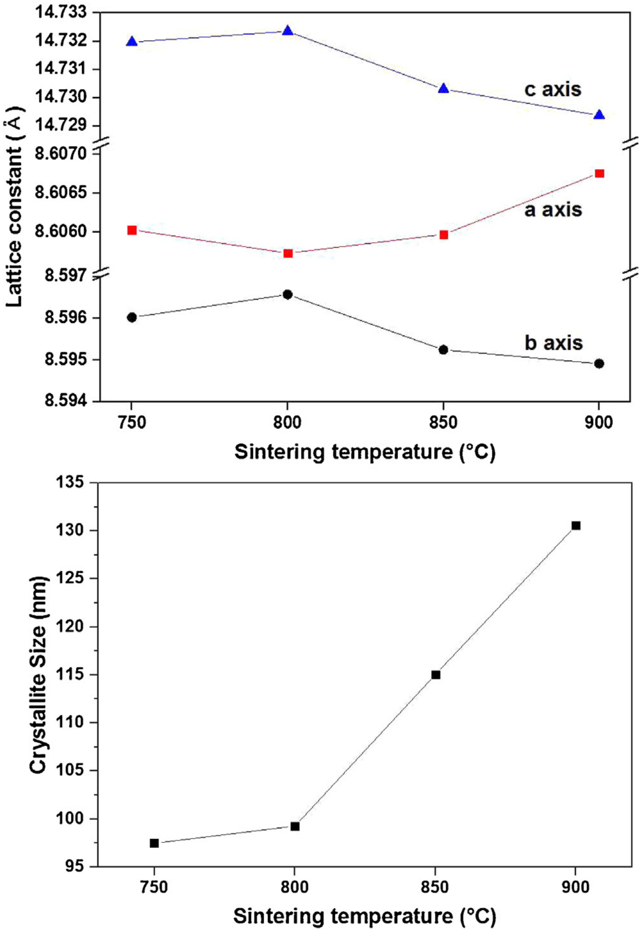

Fig. 3. Lattice constant and crystallite size of LVP/C materials by Reitveld analysis.