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V_4P_7@C nanocomposite as a high performance anode material for lithium-ion batteries

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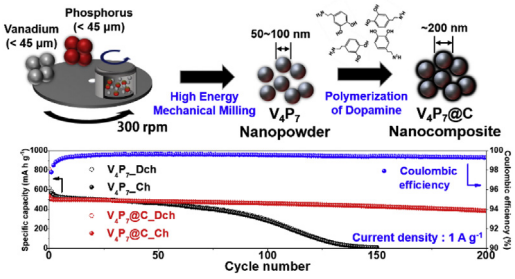
HIGHLIGHTS

- V_4P_7 is synthesized by a high energy mechanical milling as an anode for LIBs.
- V_4P_7 shows insertion reaction during lithiation by forming amorphous Li-V-P phase.
- V_4P_7 electrode delivers the high discharge capacity of 1035 mA h g^{-1} at 100 mA g^{-1}.
- V_4P_7@C shows the enhanced rate capability and high rate long-term cycle stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The V_4P_7 phase is synthesized by a facile high energy mechanical milling (HEMM) using vanadium (V) and red phosphorus (P), and its electrochemical properties and reaction mechanism as an anode for lithium ion batteries (LIBs) are investigated. As-synthesized 100 nm-sized V_4P_7 nanopowder electrode shows the insertion reaction during lithiation/delithiation by forming the amorphous Li-V-P ternary phase and delivers the high discharge and charge capacities of 1035 and 882 mA h g^{-1}, respectively, with a high Coulombic efficiency of 85% at the current density of 100 mA g^{-1}. In addition, V_4P_7 nanopowder is encapsulated with the conformal carbon layer, which is achieved through polymerization of dopamine and subsequent carbonization. As-fabricated core-shell V_4P_7@C nanocomposite electrode exhibits the much improved high rate capability and long cycle stability, delivering a high capacity of 388 mA h g^{-1} after 200 cycles at a high current density of 1 A g^{-1}, which is attributed to high electrical conductivity, high Li^+ ion mobility, and structural stability to restrict the aggregation and pulverization of active materials.

1. Introduction

Lithium-ion batteries (LIBs) are the most promising electrochemical energy storage devices for a variety of applications such as portable electronics, emerging electric vehicles (EVs), hybrid electric vehicles (HEVs), and energy storage system (ESS) [1–3]. Graphite is the most common anode material in commercial LIBs, but its specific capacity is relatively low (372 mA h g^{-1}) with a poor rate capability. Extensive efforts have been performed to develop the high performance anode materials for next generation LIBs, which include Si, alloys, metal oxides, metal phosphides, metal sulfides, and metal nitrides [4,5].

Among them, metal phosphides (MP_n) have attracted much attention as anodes for LIBs due to their high degree of electron delocalization and high-lying mixed anion-metal bands, which lead to a low oxidation state of the metal and a strong covalent character of M-P bond resulting in an overall lower insertion potential compared to their oxide

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counterparts [6]. Depending on the nature of the metal and the bonding ability of phosphorus upon Li insertion/extraction, metal phosphides are categorized into two groups [4,5];

i)insertion or intercalation reaction ($MP_y + xLi^+ + xe^- \leftrightarrow Li_xMP_y$) and ii) conversion reaction ($MP_y + 3Li^+ + 3e^- \leftrightarrow yLi_3P + M$).

The first group includes MnP_4, VP_x (x = 1, 2, or 4), FeP_2, ZnP_2, Zn_3P_2, and NiP_2, which realize the topotactic Li insertion/extraction without breaking bonds between transition metal and phosphorus. The second group includes Cu_3P, CoP_3, Sn_3P_4, NiP_2, and GaP, where the reaction between Li and MP_n results in the direct decomposition of metal phosphide into nanosized metallic particles and Li phosphide. Metal phosphides can deliver high reversible capacity between 500 and 2000 mA h g^{-1} [7–17], but low electrical conductivity and large volume change upon charge-discharge cycling are drawbacks, which require further explorations such as nano-structures or composites with conductive carbon-based materials.

In vanadium-phosphorus (V-P) system, various phases are known from metal-rich to phosphorus-rich; V_3P (tetragonal), V_2P (orthorhombic), $V_{12}P_7$ (hexagonal), V_4P_3 (orthorhombic), VP (hexagonal), V_4P_7 (tetragonal), VP_2 (monoclinic), and VP_4 (monoclinic) [18]. The first principle calculation based on the density functional theory indicates that V-P compounds (V_3P, V_2P, VP, VP_2, and VP_4) are all metallic characters, and the structure of metal-rich compound is more stable than the phosphorus-rich composition [19].

Among them, VP, VP_2, and VP_4 phases have been synthesized by high energy mechanical milling (HEMM) and their electrochemical properties have been studied as an anode for LIBs [20–22]. The VP phase showed the graphite-like topotactic intercalation reaction with lithium-ions, exhibiting high volumetric capacity and excellent cycling behavior [20]. The VP_2 compound showed the higher capacity than VP by forming the amorphous Li-V-P ternary phase during the electrochemical reaction with lithium-ions, but VP_2 suffered a rapid capacity fading [21]. The VP_4 phase sequentially reacted with lithium through topotactic lithium insertion into VP_4, phase transform from monoclinic Li_3VP_4 to cubic Li_6VP_4, decomposition to form Li_3P and VP, and another lithium insertion into VP [22].

The V_4P_7 phase, intermediate compound between VP and VP_2, has been prepared at high pressure of 35–55 kbar and its crystal structure was determined to be a PbFCl type with a space group of $P\bar{4}m2$ [23]. V_4P_7 is expected to show the intermediate electrode performance between VP and VP_2 in terms of specific capacity and cycle retention. The increased P content in the V-P system implies the higher specific capacity due to the increase of redox ion, but it may cause the cycle retention less desirable because of the larger volume expansion during lithiation/delithiation. The phosphorus-rich compound is known to be less stable than the metal-rich composition [19], which could affect the reversibility of electrochemical reaction. In spite of these expectation, V_4P_7 has not been synthesized at ambient pressure and never applied to an anode for LIBs.

In this study, V_4P_7 nanopowder was synthesized by a HEMM method using vanadium (V) and red phosphorus (P), and its electrochemical properties as an anode for LIBs were investigated. Furthermore, V_4P_7 nanopowder was encapsulated with conformal carbon to enhance the electrical conductivity and retain the structural integrity during lithiation/delithiation. The conformal carbon coating was achieved through polymerization of dopamine and subsequent carbonization. Dopamine is known to be a biomimetic adhesive polymer that can self-polymerize to form the conformal coatings on various substrates and can be converted into N-doped graphitic carbon through carbonization [24–26]. Through this novel carbon coating technology, core-shell V_4P_7@C nanocomposite was successfully fabricated and applied as an anode for LIBs.

2. Experimental

2.1. Synthesis of the V_4P_7 nanoparticles

The V_4P_7 nanopowder was prepared via high-energy mechanical milling (HEMM) method with a planetary ball mill (Pulverisette 6, Fritsch). The starting materials used for synthesis were commercial vanadium (99.95%, Alfa Aesar) and red phosphorus (98.9%, Alfa Aesar) without a further purification. Stoichiometric amount of precursor powders was placed into a hardened steel vial (80 cm^3) with hardened steel balls (diameter of 3/8 in.) at a ball-to-powder weight of 20:1 and sealed inside an argon-filled glove box. The HEMM was conducted at room temperature with a rotation speed of 300 rpm for 60 h. The final product was collected, softly ground, and stored in a glove box to minimize the surface oxidation.

2.2. Preparation of the V_4P_7@C nanocomposite

Typically, 200 mg of as-prepared V_4P_7 nanopowder was dispersed in 100 ml Tris-buffer (pH: ~8.5) by ultrasonication for 30 min. Then, 200 mg of dopamine hydrochloride was added into the solution at 25 °C and stirred for 16 h. Afterwards, the precipitates (i.e. V_4P_7@PDA nanocomposite) were obtained by centrifugation, washed three times with deionized water, and then dried at 65 °C for 12 h in air. The resulting sample was annealed at 400 °C for 2 h under N_2 atmosphere in the tube furnace (a ramping rate of 1 °C min^{-1}) and then further annealed at 500 °C for 3 h (a ramping rate of 5 °C min^{-1}).

2.3. Materials characterization

The phases of as-prepared powders and electrodes were examined by X-ray diffraction (XRD, D8-Advance, BRUKER MILLER Co.) using Cu Kα radiation (λ = 1.5406 Å). The chemical composition of as-prepared powder was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, OPTIMA 8300, Perkin-Elmer). The carbon content in the V_4P_7@C nanocomposite was measured by elemental (C, N, S) analyzer (Flash EA 1112, Thermo Electron Corporation). The morphology of the powder and electrodes were observed by field emission scanning electron microscopy (FE-SEM, SU70, Hitachi) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The ex-situ measurement of X-ray absorption near-edge structure (XANES) was carried out with a transmission mode at the 7D beamline of Pohang accelerator laboratory (PAL, Korea) in a storage ring of 2.5 GeV with a ring current of 330–360 mA.

2.4. Electrochemical measurements

The electrode was prepared by mixing 70% active material, 15% Super P carbon black, and 15% carboxymethyl cellulose (CMC) binder by weight to form a slurry, which was coated on the copper foil and followed by drying in a vacuum oven at 65 °C overnight. The electrode was punched into a round disk with 1.5–2 mg cm^{-2} loading of active material and then kept in the vacuum oven at 70 °C for 12 h. The CR2032 coin cell was fabricated inside an argon-filled glove box by employing poly-propylene (Welcose, Korea) separator and lithium foil counter/reference electrode. The electrolyte used was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (1:1:1 v/v) with the addition of 2 vol% of vinylene carbonate (VC) additive. Galvanostatic cycling test was performed with a battery testing system (Wonatech, Korea) within a voltage range of 0.01–2 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) experiment was carried out at a frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 5 mV using an impedance analyzer (Zive, SP1). For the ex-situ XRD, SEM and TEM analyses, the electrode materials were collected by disassembling the test cell in the argon-filled glove box, rinsing with DMC several times, and drying at