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# $Li_3V_2(PO_4)_3$/graphene nanocomposite as a high performance cathode material for lithium ion battery

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## Abstract

In this work, pure LVP nanoparticles and an LVP/graphene nanocomposite are successfully synthesized by a simple and cost effective polyol based solvothermal method, which can be easily scaled up. The synthesized nanocomposite contained small (30–60 nm) LVP nanoparticles completely and uniformly anchored on reduced graphene nanosheets. As a cathode for lithium ion batteries, the nanocomposite electrode delivered high reversible lithium storage capacity (189.8 mA h $g^{-1}$ at 0.1 C), superior cycling stability (111.8 mA h $g^{-1}$ at 0.1 C, 112.6 mA h $g^{-1}$ at 5 C, and 103.4 mA h $g^{-1}$ at 10 C after 80 cycles) and better C-rate capability (90.8 mA h $g^{-1}$ at 10 C), whereas the pure LVP nanoparticles electrode delivered much less capacity at all investigated current rates. The enhanced electrochemical performance of the nanocomposite electrode can be attributed to the synergistic interaction between the uniformly dispersed LVP nanoparticles and the graphene nanosheets, which offers a large number of accessible active sites for the fast diffusion of Li ions, low internal resistance, high conductivity and more importantly, accommodates the large volume expansion/contraction during cycling.

*Keywords:* Cathode; Graphene; Lithium ion battery; Lithium vanadium phosphate; Solvothermal

## 1. Introduction

Lithium ion secondary batteries are considered the most efficient energy storage systems of high energy density and long lifetime especially as plug-in hybrid electric vehicles (HEV) and electric energy (EV) storage systems for solar and wind energy sources [1]. The cathode material plays a crucial role in determining the power density and safety of a battery. Lithium cobalt oxide was the first to be utilized as a positive electrode material for commercial lithium ion secondary batteries, but its high cost, toxicity and poor capacity at high current rates prohibit its use in large-scale applications, such as EVs and HEVs. Recently, polyanion-type materials, such as $LiMPO_4$ (M = Fe, Co, Ni, and Mn) [2–7] and $Li_3V_2(PO_4)_3$ [8,9], have been discovered as potential cathode materials for rechargeable lithium ion batteries in large-scale applications. Among these, the monoclinic lithium vanadium phosphate, $Li_3V_2(PO_4)_3$ (LVP), is regarded as one of the most promising cathode materials for high-power lithium-ion batteries because of its high energy density, high theoretical capacity, good $Li^+$ mobility, and excellent thermal and cyclic stabilities and high safety [10–12]. In the monoclinic LVP, all three lithium ions can be completely extracted from the lattice at an applied voltage in the range of 3.0–4.8 V based on the $V^{3+}/V^{4+}$ and $V^{4+}/V^{5+}$ redox couples, giving a theoretical capacity of as high as 197 mA h $g^{-1}$. Nevertheless, the extraction of the third lithium ion at 4.55 V is kinetically the most difficult and is coupled with a significant overvoltage [13–15]. Therefore, LVP is also cycled at an applied voltage in the range of 3.0–4.3 V, resulting in a theoretical capacity of 133 mA h $g^{-1}$. More importantly, the monoclinic-phase LVP has a three-dimensional framework, with $VO_6$ octahedra and $PO_4$ tetrahedra sharing oxygen vertices, which degrades electronic conductivity and high rate discharges [16]. Furthermore, LVP has low intrinsic electronic conductivity ($2.4 \times 10^{-7}$ S $cm^{-1}$) [17], which greatly limits its practical application. To overcome this disadvantage and enhance the rate capability of

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LVP, various methods have been employed in the past few years: doping with foreign atoms [16,18–21], decreasing the particle size [8,22] and carbon coating [23–29]. Carbon coating is simple and efficient for enhancing the electrical conductivity of LVP, although increased carbon content, significantly decreases the tap density and energy density of LVP [30]. In addition, it is rather difficult to homogenously encapsulate LVP with a carbon shell during the synthesis of LVP at high-temperature, which would decrease the charge/discharge capacities at higher current rates. Therefore, the performance of an LVP based cathode needs to be improved.

Compared to traditional carbon, graphene nanosheets, a single-atom-thick sheet of honeycomb carbon lattice, show a number of intriguing unique properties, such as superior electrical conductivity, high surface area, large surface-to-volume ratio, and good mechanical properties [31–33]. Recently, improved cycling stability and rate performances were reported when an electrode material was supported by graphene [34,35]. In the present study, an LVP/graphene nanocomposite was synthesized by a solvothermal method using polyol, wherein LVP nanoparticles are fully enwrapped in the 2D network of the graphene layer, which effectively connects the particles together. Therefore, the efficiency of graphene nanosheets to wrap or coat the nanoparticles is higher than that of conventional carbon. Because of this higher efficiency, even a small amount of graphene in the nanocomposite can greatly improve the rate performance and cycling stability. In addition, the polyol process also has many advantages since it allows nanoscale synthesis at apparently low synthesis temperatures and allows short-term heat treatment. Furthermore, the polyol medium appears to have multi-purpose roles as a solvent and stabilizer, which limit the growth of the particles and actively suppress particles agglomeration in the development of fine LVP. However, in the synthesized nanocomposite, the graphene nanosheets and LVP nanoparticles, connected to each other, facilitate fast electron and $Li^+$ ion transport and exhibit high specific capacity, excellent cycling stability and rate capability at all investigated C-rates compared with pure LVP nanoparticles.

## 2. Experimental

### 2.1. Preparation of graphene oxide and graphene nanosheets

In a typical synthesis method, graphene oxide (GO) is first synthesized by the modified Hummers method [36], and the obtained GO colloidal suspension is kept for a long time at room temperature. The obtained GO is then reduced to graphene nanosheets by the polyol-based reduction method. The detailed preparation procedure for the reduction of graphene nanosheets can be found in our previous papers [37,38].

### 2.2. Material synthesis

LVP/graphene nanocomposite and pure LVP samples were prepared in polyol medium by a low-cost solvothermal method using lithium acetate dihydrate ($CH_3COOLi \cdot 2H_2O$, $\geq 99\%$, Aldrich), vanadium acetyl-acetonate ($C_{15}H_{21}O_6V$, 97%, Aldrich), and phosphoric acid ($H_3PO_4$, $\geq 85\%$, Daejung) as precursor materials. Diethylene Glycol (DEG) {$C_4H_{10}O_3$, 99%, Daejung Chemicals, South Korea} was used as a solvent. Initially, a stoichiometric amount of vanadium acetyl-acetonate and lithium acetate dihydrate was dissolved into 30 ml of DEG and stirred for 24 h. After that, the calculated amount of phosphoric acid was added into the solution and again stirred for 24 h to obtain a clear suspension. At the same time, 20 wt% of the obtained reduced graphene nanosheets was also added to the mixed solution to allow the nanoparticles to anchor onto the reduced graphene nanosheets. After obtaining a homogenous solution, the resulting solution was sealed in a 40 ml Teflon-line bomb and placed into a drying oven pre-heated at 235 °C, where it was kept at that temperature for 16 h. After cooling and ultra-sonication, the resulting precipitates were washed with acetone and methanol several times to remove residual organic constituents before filtering using ceramic membrane funnels and drying in a vacuum chamber for 12 h at 120 °C. The obtained sample was thoroughly ground using an agate mortar and annealed at 750 °C for 6 h under nitrogen atmosphere to increase the crystallinity of the sample. For comparison, a pure LVP sample was also synthesized and annealed under the same synthesis conditions as the LVP/graphene nanocomposite without the addition of graphene nanosheets.

### 2.3. Surface and morphology characterizations

The crystal structures of the LVP/graphene nanocomposite and pure LVP samples were characterized by X-ray diffraction (XRD, Shimadzu X-ray diffractometer) using Cu Kα radiation ($\gamma$=1.5406 Å). The morphology and sizes of the particles were determined by field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi) and field-emission transmission electron microscopy (FE-TEM, Philips Tecnai F20 at 200 kV accelerating voltage, KBSI, Chonnam National University, South Korea). The samples were soaked in ethanol and dispersed by ultrasonic vibration before coating onto copper grids for FE-TEM examination. The carbon contents of both the annealed samples (pure LVP nanoparticles and LVP/graphene nanocomposite) were determined by CHN elemental analysis using Flash-2000 Thermo Fisher. The Raman measurement of the LVP/graphene nanocomposite was conducted on a LabRam HR800 UV Raman Microscope (Horiba Jobin-Yvon, France, KBSI, Gwangju Centre), using 514 nm (10 mW) laser excitation. The spectra were recorded in 800–2000 $cm^{-1}$ range with accumulated scans for an enhanced resolution. The annealed sample of LVP/graphene nanocomposite was examined by X-ray photoelectron spectroscopy (XPS) using a Thermo VG Scientific instrument, Multilab 2000 in order to establish the valence states of vanadium (V), phosphorus (P) and oxygen. XPS measurements were carried out using a dual anode X-ray source Al Kα radiation ($h\nu$=1486.6 eV). The spectrometer was calibrated with respect to the C1s peak (binding energy 285.02 eV).

### 2.4. Electrochemical measurements

Cathode electrodes were fabricated by mixing the active material (80 wt%) with super-P (10 wt%) and polyvinylidene fluoride