



Pomegranate-like Li_3VO_4 /3D graphene networks nanocomposite as lithium ion battery anode with long cycle life and high-rate capability



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ABSTRACT

Li_3VO_4 anchored 3D graphene networks (Li_3VO_4 /3DGNs) nanocomposite was constructed via a facile one-pot hydrothermal method. The as-prepared Li_3VO_4 /3DGNs nanocomposite exhibits a unique pomegranate-like structure where nanohole-dotted Li_3VO_4 nanoparticles resembling pomegranate seeds are firmly anchored and uniformly distributed on 3DGNs. Li_3VO_4 /3DGNs composite presents excellent cycling and rate performance. The initial reversible capacity is 397 mAh g^{-1} at 2 A g^{-1} and remains at 259 mAh g^{-1} even after 2500 cycles. In addition, under current densities of 0.2, 0.4, 0.8, 2, 4, 8, 16 and 32 A g^{-1} , the composite delivers large capacities of 471, 404, 359, 318, 290, 247, 191 and 142 mAh g^{-1} , respectively. The excellent electrochemical performance is mainly attributed to the enhanced electrical conductivity and structural stability as well as accelerated Li^+ diffusion derived from both the 3D continuous conductive channels endowed robust 3DGNs and the nanohole-dotted Li_3VO_4 nanoparticles.

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1. Introduction

Lithium-ion batteries (LIBs) are one of the most successful portable energy storage devices in modern society due to their high energy density and environmentally friendly characteristics. However, graphite, the most widely applied commercial anode in LIBs, encounters several demerits such as unsafe Li^+ intercalation voltage ($\sim 0.2 \text{ V}$), low theoretical capacity (372 mAh g^{-1}) and limited rate capability [1–3]. Many efforts have been devoted to finding substitutes for graphite. Among all currently studied anode materials [4–9], anode materials based on intercalation/de-intercalation mechanism have attracted considerable interests for practical application since they can normally conserve structural integrity after repeated Li^+ insertion/extraction [10–12].

Li_3VO_4 , a novel anode material based on intercalation/de-intercalation mechanism, is currently considered as a promising anode candidate over graphite due to its high Li^+ mobility ($\approx 10^{-4} \text{ S m}^{-1}$), safe and energy-efficient Li^+ intercalation voltage range of 0.5–1.0 V as well as high theoretical capacity of 394 mAh g^{-1} [13,14]. Nevertheless, the electronic conductivity of Li_3VO_4 is low, which would lead to a large polarization of the

electrode during the charge-discharge process especially under high current density, thus inevitably compromising the high-rate capability and long-term cycling stability of Li_3VO_4 anode [13]. To overcome this problem, approaches of combining poorly conductive Li_3VO_4 with conductive carbon matrix have been adopted recently. For example, a Li_3VO_4 /graphite composite synthesized via a quasi sol gel method [15] exhibits improved rate performance. Rate capacities of 364, 278 and 203 mAh g^{-1} are obtained at current densities of 0.5, 1.2 and 2.3 A g^{-1} for Li_3VO_4 /graphite, while those for pure Li_3VO_4 are only around 140, 100 and 70 mAh g^{-1} at 0.4, 0.8 and 2 A g^{-1} [16]. The enhanced rate performance may be ascribed to the decrease of charge transfer resistance resulted from the good electrical contact between Li_3VO_4 and graphite. However, at high rates, for example, 12 A g^{-1} , the capacity of Li_3VO_4 /graphite fades to below 50 mAh g^{-1} . The agglomeration of Li_3VO_4 particles is believed to be responsible for the capacity deterioration at high rates since the as-formed large aggregates with sizes of more than $5 \mu\text{m}$ would impede the fast transportation of electrons and Li ions. Hence, inhibiting particle agglomeration to acquire small-sized Li_3VO_4 particles while keeping the good conductivity is the key for enhancing the high-rate performance of Li_3VO_4 [13,14]. Compared with graphite or amorphous carbon, reduced graphene oxide nanosheets (rGOs/GNS) are rich in oxygen-containing functional groups, which can serve as preferred anchoring sites for Li_3VO_4 particles via strong chemical interactions to suppress their

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agglomeration, thus generally obtaining small-sized Li_3VO_4 particles [17–20]. For example, in the composite of Li_3VO_4 @GNS [21], most of the Li_3VO_4 particle sizes are reduced to less than 100 nm, but some of them still exceed 500 nm. The reason for the particle aggregation maybe the heavy restacking of GNS, which leads to the loss of many available surface interaction sites between Li_3VO_4 and GNS [22]. Previous studies [23–25] on graphene have demonstrated that the assembly of GNS into three dimensional graphene networks (3DGNs) is an effective approach to circumvent the restacking of GNS, thus possibly providing more active sites for anchoring Li_3VO_4 particles and suppressing their agglomeration. Beyond that, the interconnected structure of 3DGNs has two more merits compared with GNS: first, it can provide 3D continuous conductive electron transfer channels inside 3DGNs, thus further facilitating the charge transfer inside the composite [23]. Second, intrinsically robust 3D frameworks of 3DGNs can accommodate lattice strain/stress caused by Li^+ insertion/extraction upon continuous cycling [17]. Therefore, it is reasonable to speculate that combining Li_3VO_4 nanoparticles with 3DGNs is an effective way to further improve the high-rate and long-term cycling performance of Li_3VO_4 .

In this work, a unique pomegranate-like Li_3VO_4 /3DGNs nano-composite was synthesized via a facile one-pot hydrothermal method. As an anode for LIBs, this composite delivers a high rate capacity of 142 mAh g^{-1} at 32 A g^{-1} . Meanwhile, at a current density of 2 A g^{-1} , a capacity as high as 259 mAh g^{-1} can still be obtained even after 2500 cycles.

2. Experimental

2.1. Mixture preparation

Graphene oxide (GO) was prepared from natural graphite (Hengdeli, $20 \mu\text{m}$, 99% carbon basis) by a modified Hummers method [26]. Dried GO was then dissolved in deionized water via sonication to prepare 3 mg mL^{-1} GO solution. The synthesis process of Li_3VO_4 /3DGNs is illustrated in Fig. S1. $0.468 \text{ g NH}_4\text{VO}_3$ and 1.68 g LiOH were dissolved in 50 mL GO solution using magnetic stirring and ultrasound. The resultant mixture was then transferred to a 100 mL Teflon-lined autoclave and kept at $180 \text{ }^\circ\text{C}$ in a high temperature oven for 11 h. Next, the as-prepared solid product was separated from the autoclave and washed four times (8000 rpm , 5 min each time) in a centrifugal machine (Kaite TGL16M). For the first two times, the product was washed with deionized water (30 mL each time) in a 50 mL centrifugal tube. For the next two times, the product was washed with tertiary butanol (30 mL each time) in a 50 mL centrifugal tube. The product was then freeze-dried for 24 h. The prepared product is noted as Li_3VO_4 /3DGNs composite and content of 3DGNs in the Li_3VO_4 /3DGNs composite is detected to be 10.1 wt% by thermogravimetric analysis as shown in Fig. S2. For comparison, pure Li_3VO_4 was prepared via the same hydrothermal method by mixing $0.468 \text{ g NH}_4\text{VO}_3$ and 1.68 g LiOH in 50 mL deionized water instead of GO solution. 3DGNs were also prepared by the same hydrothermal method using 50 mL GO solution without NH_4VO_3 and LiOH . The optical and SEM images of 3DGNs are shown in Fig. S3. Subsequently, a reference sample named $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture was prepared by simply grinding pure Li_3VO_4 powder and 3DGNs at a weight ratio of 9:1.

2.2. Material characterization

To investigate the phase components and structures, X-ray diffraction (XRD) was carried out on an X-ray diffractometer (D2 PHASER, Bruker AXS). The morphology and microstructure of the samples were investigated by field emission scanning electron

microscopy (FESEM, LEO 1530 Gemini) and transmission electron microscopy (TEM, FEI Tecnai G² F30 S-Twin). Raman spectra were measured by a LabRAM HR800 spectrograph to characterize the structure of the samples and understand their electron behaviours.

2.3. Electrochemical measurements

Electrochemical measurements were performed using Swagelok-type cells. The preparation process of the working electrodes was consisted of three steps. First, active material, Super P and PVDF were mixed applying a weight ratio of 75:20:5 and grounded in a mortar for 0.5 h. Then, a slurry was prepared using *N*-methylpyrrolidinone (NMP) and coated onto a Cu foil using the doctor blade technique. Next, the electrode was dried in a vacuum oven at $120 \text{ }^\circ\text{C}$ for 12 h to remove NMP and water. Mass loading of active material on Cu current collector was $0.9\text{--}1.2 \text{ mg cm}^{-2}$. The Swagelok-type cells were assembled in a glove box filled with argon atmosphere ($<1 \text{ ppm}$, H_2O and O_2) by applying a Whatman GF/D borosilicate glass-fibre sheet as the separator, a lithium pellet as the anode, and 1 M LiPF_6 dissolved in a solution of ethylene carbonate/dimethyl carbonate (1:1 in volume) as the electrolyte. Assembled cells were allowed to soak for 12 h before electrochemical tests. Charge/discharge measurements were carried out between 3.0 V and 0.2 V on an automatic battery testing system (CT2001A, LANHE). Electrochemical impedance spectroscopy (EIS) measurements were carried out after 5 cycles in a frequency range of $0.01\text{--}100 \text{ kHz}$ with AC signal amplitude of 5 mV on a CHI 660e electrochemical workstation. Cyclic voltammetry (CV) measurements were also carried out on the CHI 660e electrochemical workstation at a scan rate of 0.05 mV s^{-1} between 0.2 and 3.0 V . All electrochemical measurements were carried out under room temperature.

3. Results and discussion

Fig. 1(a) presents the XRD patterns of the Li_3VO_4 /3DGNs composite and the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture. Diffraction peaks of the Li_3VO_4 /3DGNs composite and the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture can be indexed into an orthorhombic Li_3VO_4 phase (JCPDS No. 38–1247). The typical (002) peak of graphene at 26° is not detected in both samples, which may be eclipsed by the (111) peak of Li_3VO_4 . Raman spectra in Fig. 1(b) confirm the existence of Li_3VO_4 and graphene in the Li_3VO_4 /3DGNs composite and the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture. Peaks located between 200 and 500 cm^{-1} and $750\text{--}950 \text{ cm}^{-1}$ correspond to the Raman peaks of Li_3VO_4 and peaks in ranges of $1250\text{--}1470 \text{ cm}^{-1}$ and $1490\text{--}1660 \text{ cm}^{-1}$ can be attributed to the D band (sp^3 hybridization) and G band (sp^2 hybridization) of graphitic carbon. From the insert picture in Fig. 1(b), two features can be summarized: i) the peak intensity ratios between peaks of D band and G band (I_D/I_G) of the Li_3VO_4 /3DGNs composite, the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture and pure 3DGNs are estimated to be 1.02, 1.05 and 1.15, respectively. The smaller I_D/I_G ratio indicates an enhanced graphitization degree of 3DGNs, possibly suggesting the improvement of electron transfer properties [27,28]; ii) the peak of the G Raman band of graphene in the Li_3VO_4 /3DGNs composite is observed to be blue-shifted from 1576 cm^{-1} for 3DGNs to 1588 cm^{-1} by 12 cm^{-1} , while that for the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture remains at 1576 cm^{-1} . This blueshift of the peak of G Raman band in the Li_3VO_4 /3DGNs composite is attributed to the enhanced charge transfer from Li_3VO_4 to 3DGNs [29,30], indicating that better electrical contact between Li_3VO_4 and 3DGNs is achieved via the *in situ* co-growth of these two components.

The morphologies of the Li_3VO_4 /3DGNs composite and the $\text{Li}_3\text{VO}_4 + 3\text{DGNs}$ mixture are compared in Fig. 2. From the low magnification SEM image of the Li_3VO_4 /3DGNs composite in

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