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Polystyrene-template-assisted synthesis of Li₃VO₄/C/rGO ternary composite with honeycomb-like structure for durable high-rate lithium ion battery anode materials



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ABSTRACT

Li₃VO₄/C/rGO (HC-LVO/C/G) ternary composite with honeycomb-like structure is successfully prepared through a simple spray drying method with polystyrene (PS) microspheres as soft template. In this characteristic structure, carbon-coated Li₃VO₄ nanoparticles are well wrapped by rGO sheets and uniformly distributed within the honeycomb-like micrometer-sized clusters. The double coating layers of amorphous carbon and rGO can avoid the direct exposure of Li₃VO₄ nanoparticles to the electrolyte and enhance the electronic conductivity. Meanwhile, the honeycomb-like structure can shorten the diffusion paths of Li⁺ ions and favors the relaxation of the strain/stress during cycling. The resultant HC-LVO/C/G composite exhibits significantly improved high-rate performance and long cycle-life (the high reversible capacity of 312 mAh g⁻¹ can be maintained after 1000 cycles at 10 C) compared with the contrastive Li₃VO₄/C composite synthesized by a typical solid-state reaction method.

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1. Introduction

Lithium ion batteries (LIBs) have been successfully commercialized and widely used in consumer electronics during the last two decades due to their high energy density [1,2]. However, the current state-of-the-art LIBs using graphite as anode still can not satisfy the demand of large-scale application such as energy storage for smart grids and electric vehicles [3]. Both rate capability and safety are the critical criterions for large-scale application [4]. Although graphite has a high electronic conductivity, the much lower ionic conductivity limits its high-rate performance. Moreover, the relatively low Li⁺ ions insertion potential (<0.2 V vs Li⁺/Li) may cause serve safety issue due to the growth of dendritic lithium especially during rapid charge/ discharge [5,6]. Thus, developing alternative anode materials with good rate performance and high safety has become an urgent task for the practical large-scale LIB application.

Recently, β form Li₃VO₄ has been studied as a new high-safety anode material for LIBs [7–9]. Li₃VO₄ possesses the theoretical capacity of 394 mAh g⁻¹, which is close to that of graphite

http://dx.doi.org/10.1016/j.electacta.2017.06.108 0013-4686/© 2017 Elsevier Ltd. All rights reserved. (372 mAh g^{-1}) [10]. Meanwhile, the safer operating voltage (mainly between 0.5 ~ 1.0 V vs Li⁺/Li) can intrinsically avoid the formation of surface Li-plating [11]. Due to the relatively high specific capacity and good safety, Li₃VO₄ can be a promising anode candidate for large-scale LIB application [12,13]. Despite those predominant features, the practical application of Li₃VO₄ are not realized yet owing to two main obstacles. One is its low electronic conductivity. Another is the unsatisfactory effective diffusion rate of Li⁺ ion, which is dramatically limited by particle size and specific area of materials in the real condition, in spite of the relatively high theoretical Li⁺ ion diffusion coefficient of Li₃VO₄ [14,15].

Two main types of approaches have been proved to overcome these intractable problems effectively. One feasible route is to hybridize with carbon materials such as amorphous carbon [8,16–18], carbon nanotubes (CNTs) [19,20], and graphene [21–23]. These Li₃VO₄/C composites can enhance the electronic conductivity effectively. Another popular strategy is to construct nano-sized or hollow structured Li₃VO₄, which can shorten the Li⁺ ions diffusion path and increase the electrode/electrolyte contact area leading to higher diffusion rate of Li⁺ ions [10,24–27].

Herein, we aim to achieve rapid ionic and electronic transport simultaneously based on a highly conductive honeycomb-like architecture. As shown in Fig. 1, with the assistance of polystyrene



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Fig. 1. The preparation procedure of the HC-LVO/C/G composite.

(PS) microsphere as the soft template, glucose as the carbon source and reduced graphene oxide (rGO) as the supporting matrix, the Li₃VO₄/C/rGO ternary composite (HC-LVO/C/G) with honeycomblike structure was successfully synthesized by one-pot spray drying method and subsequent heat treatment. The rational architecture offers several advantages as high-rate performance LIB anodes: (a) the carbon coating layer can effectively enhance the electronic conductivity. (b) the honeycomb-like architecture with many voids can provide perfect 3D pathways for Li⁺ ions diffusion and accommodate the volume change during cycling. (c) The highly conductive and flexible rGO sheets serving as support matrix can further maintain the electrical and structural integrity of the composite. The contrastive Li₃VO₄/C (LVO/C) composite was also synthesized by a typical solid-state reaction method. Owing to the rational structure design, the resultant HC-LVO/C/G composite exhibits significantly enhanced electrochemical performance compared to LVO/C.

2. Experimental section

2.1. Synthesis of PS emulsion solution

Before the polymerization, certain amount of styrene was washed with the same volume of sodium hydroxide solution (4 mol L^{-1}) to remove the anti-polymerizer using a separatory funnel and then washed with deionized water until the pH value of the raffinate was 7.0. In a typical experiment, 0.152 g sodium lauryl sulfate (SDS), 0.305 g potassium persulfate (KPS) and 140 mL alcohol-water solution (2:5 v/v) were put into a 250 mL three-neck flask. After stirring under N₂ atmosphere for 0.5 h, the solution was heated to 70 °C for 10 minutes. Then the treated styrene of 7.0 mL was added into the solution and heated at 70 °C for 10 h with vigorous stirring. The as-prepared PS emulsion solution was stored for the later use.

2.2. Synthesis of HC-LVO/C/G and LVO/C composites

In a typical experiment, 0.520 g of V_2O_5 , 0.633 g of Li_2CO_3 , 0.5 g of Glucose, 7.5 g of GO aqueous suspension (wt% = 2%, Shanghai Ashine Technology Development Co., Ltd) and 20 mL of PS emulsion solution were added into 80 mL distilled water and

stirred overnight. The mixture was spray dried by using a B-290 mini spray dryer (Buchi Co., Switzerland). The inlet temperature was 210 °C, and the pump rate was 10%. The spray dried precursor was collected and subsequently calcined at 600 °C for 10 h at the heating rate of 5 °C min⁻¹ under the Ar atmosphere to generate the final HC-LVO/C/G composite. The contrastive LVO/C composite was synthesized by a typical solid-state reaction method [16]. 0.520 g of V_2O_5 , 0.633 g of Li_2CO_3 and 0.5 g of Glucose were thoroughly mixed by using an agate mortar. The mixture was pre-calcined at 350 °C for 5 h, then calcined at 750 °C for 8 h under an Ar/H₂ (90/10 v/v) atmosphere with the heating rate of 5 °C min⁻¹ to obtain the LVO/C composite.

2.3. Materials characterization

Morphological analysis of composites was carried out by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi), high-resolution transmission electron microscopy (HRTEM, JEOL-2100) and (FEI, TECNAI G2 F30). The X-ray diffraction (XRD) data were recorded at the Rigaku miniflex 600 X-ray diffractometer, using Cu K α radiation. Raman spectra were collected on the inVia Raman microscope (Renishaw) equipped with the 532 nm Ar-ion laser. The carbon content of the composites was measured by using the VARIO EL III element analysis instrument (Elementar Co., Germany).

2.4. Electrochemical measurement

The working electrodes consisted of the active material, acetylene black, vapor-grown carbon fiber (VGCF) and polyvinylidene fluoride (PVDF) with the mass ratio of 70:15:5:10. The mixture was stirred thoroughly in N-methyl-2-pyrrolidone (NMP) and casted onto an Cu foil to prepare the electrode film, which was then dried at 80 °C under vacuum overnight. The typical loading mass of active material was about 0.69 mg cm⁻². The working electrodes were assembled into CR-2016 coin cells in an Ar-filled glovebox. An electrolyte solution consisting of 1.0 M LiPF₆ in the mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (v/ v=1:1) was used. Li foil was used as the counter electrode, and Celgard 2400 microporous polypropylene membrane was used as the separator. For full cell assembly, LiCoO₂ was used as the



Fig. 2. (a) XRD patterns of LVO/C and HC-LVO/C/G composites. (b) Raman spectra of pristine LVO, LVO/C and HC-LVO/C/G composites.

cathode. The anode is limited and the capacity of full cell was calculated based on the mass of the HC-LVO/C/G electrode. Galvanostatic cycling tests were performed on a battery testing system (Neware BTS battery charger, Shenzhen, China). Electrochemical impedance spectra (EIS) results were obtained at the electrochemical workstation of Autolab PGSTAT 302N. The frequency applied was from 10 mHz to 100 kHz.

2.5. Calculation procedure

All structure relaxations and volume calculations for Li_3VO_4 , Li_5VO_4 and Li_6VO_4 were finished by the Vienna Ab-initio Simulation Package (VASP) [28]. The GGA+U framework with the Projector Augmented Wave (PAW) pseudopotential was used in the calculations [29]. The PBE form of the exchange-correlation functional was chosen [30]. For the DFT+U calculations, we followed the simplified rotationally invariant form that is proposed by Dudarev [31]. According to Arroyo-de et al., the U was fixed to 4 eV and the J was fixed to 1 eV. A constant value of 600 eV was used as the energy cut off [32]. Throughout the calculations, spin polarized calculations were performed.

3. Result and discussion

The schematic illustration for the preparation of the HC-LVO/C/ G composite is shown in Fig. 1, and the synthetic details were presented in the experimental section. First micro-sized droplets containing Li₂CO₃, V₂O₅, glucose, GO and PS microspheres (Fig. S1) were produced by using a nozzle. Then the droplets underwent solvent evaporation and solute condensation to form hollow structured microspheres decorated with PS particles. After annealing, the depolymerization of PS soft template produced the honeycomb-like structured $Li_3VO_4/C/rGO$ ternary composite.

The XRD patterns of HC-LVO/C/G and LVO/C composites are shown in Fig. 2. The diffraction peaks of both samples can be well indexed to the electrochemically active orthorhombic Li₃VO₄ (space group Pnm21, ICPDS No. 38-1247) [33]. Raman spectra of both LVO/C and HC-LVO/C/G composites exhibit two characteristic bands for carbonaceous materials near 1345 cm^{-1} and 1591 cm^{-1} corresponding to D-band (in-plane vibrations of strong disorder carbon) and G-band (graphitic carbon), respectively [34,35]. For the LVO/C, the small peaks between 800 cm^{-1} and 1000 cm^{-1} are observed, which are in good agreement with the pristine Li₃VO₄ [36]. But for the HC-LVO/C/G, the intensity of these corresponding peaks decreases seriously. Only a very weak peak at about 820 cm^{-1} (inset in Fig. 2b) is noticed, owing to the fact that most of the laser signal is absorbed by the double coating layers of amorphous carbon and rGO sheets on the surface of LVO particles [22]. The carbon content in the LVO/C and HC-LVO/C/G composites are measured to be 12.12% and 17.62%, respectively.

Theoretical calculation is used to simulate the volume change of Li_3VO_4 during Li^+ ions insertion. Calculated crystal-structure of pristine Li_3VO_4 fit well with the XRD data. It means that the method and model are reliable and can be used to calculate the structures. As shown in Fig. 3 and Table 1, the calculation results show that the theoretical volume expansion is 4.7% and 16.9% when it is inserted with Li^+ ions corresponding to Li_5VO_4 and Li_6VO_4 , respectively. In this work, the reversible capacity of 387 mAh g⁻¹ should be equivalent to 2 Li^+ ions insertion. But even volume expansion of 4.7% is relatively small, it may still decrease the crystallinity of Li_3VO_4 and cause Li_3VO_4 particles cracking especially during high-rate cycling, which has been observed in



Fig. 3. View of the optimized crystal structure of Li₃VO₄, Li₅VO₄ and Li₆VO₄.

Table 1

Crystal-structure simulation results of $\rm Li_3VO_4, Li_5VO_4$ and $\rm Li_6VO_4$ obtained by using the VASP method.

Structure	a, b, c (Å)	α, β, γ	Cell Volume (Å ³)
Li ₃ VO ₄ (XRD)	6.3272, 5.4471, 4.9483	90, 90, 90	170.54
Li_3VO_4	5.01192, 5.48372, 6.36231	90.0, 90.0, 90.0	174.86
Li ₅ VO ₄	5.24610, 5.68740, 6.14169	90.0, 90.0, 93.0	183.00
Li ₆ VO ₄	5.28183, 5.43497, 7.12309	90.0, 88.4, 89.9	204.40

other previous reports [7,21,26,37,38]. This characteristic honeycomb-like structure with many voids may favor the relaxation of the strain/stress and the maintenance of crystalline structure during cycling.

The low magnification SEM image of the HC-LVO/C/G composite (Fig. 4a) shows well-dispersed and sphere-shaped particles with particle size ranging from about 1 μ m to 7 μ m. Many voids derived from the depolymerization of PS template can be observed in the



Fig. 4. (a, b) SEM images of the HC-LVO/C/G composite. (c, d) TEM images of the HC-LVO/C/G composite. (e, f) HRTEM images of the HC-LVO/C/G composite. (g) STEM image and corresponding element mapping of a single HC-LVO/C/G composite particle.



Fig. 5. (a) Nitrogen adsorption-desorption isotherms and (b) pore-size distributions of LVO/C and HC-LVO/C/G composites.



Fig. 6. Typical galvanostatic charge-discharge curves of (a) HC-LVO/C/G and (b) LVO/C composites at 0.5 C ($1 C \approx 0.4 \text{ Ag}^{-1}$). (c) Capacity retention and Coulombic efficiency of HC-LVO/C/G and LVO/C composites at 0.5 C (d) Rate performance of HC-LVO/C/G and LVO/C composites at various current densities from 0.5 C to 100 C. (e) Long-term cycling performance of HC-LVO/C/G and LVO/C composites at 10 C.

hollow microspheres (Fig. 4b, c and g) to form the honeycomb-like structure. The composite cluster is made of many LVO nanoparticles with the size of about 80 nm well wrapped by the rGO sheets (Fig. 4d). The double coating layer of amorphous carbon layer combined with rGO sheets (wrinkles in Fig. 4e) can be obviously seen on the surface of LVO nanoparticles. The HRTEM image (Fig. 4f) corroborates the presence of the double coating layer, and clear lattice fringes with a spacing of 0.41 nm, corresponding to the (110) planes of orthorhombic LVO, can be also distinguished inside. The elemental mappings of C, O and V (Fig. 4g) evidently indicate that LVO nanoparticles are uniformly distributed throughout the carbon matrix.

Fig. 5a shows the Nitrogen adsorption-desorption isotherms of LVO/C and HC-LVO/C/G composites. Compared to the LVO/C, the

nitrogen adsorption isotherms of HC-LVO/C/G exhibit a typical type-IV adsorption curve, indicating the presence of porous structure. The pore-size distribution of HC-LVO/C/G (Fig. 5b) shows a narrow peak centering at ~3.0 nm (the mesopores attributed from the amorphous carbon and rGO) and another broad peak at ~100 nm (the macropores generated from PS template). The specific surface of the HC-LVO/C/G is $122.4 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $0.36 \text{ cm}^3 \text{ g}^{-1}$. When compared against the values of the LVO/C ($58.5 \text{ m}^2 \text{ g}^{-1}$ and $0.047 \text{ cm}^3 \text{ g}^{-1}$, respectively), the increased surface area and hierarchical porous structure of the HC-LVO/C/G are beneficial for the penetration of electrolyte, leading to faster diffusion of Li⁺ ions [39].

Fig. 6a and b illustrate the typical charge-discharge curves of HC-LVO/C/G and LVO/C composites at 0.5 C within the potential



Fig. 7. (a) Electrochemical impedance spectra (EIS) and fitting results of the HC-LVO/C/G and LVO/C composites electrodes after 1 cycle. (b) Dependence of the real impedance (Z') on the reciprocal of the square root of the frequency ($\omega^{-1/2}$) for determination of the Warburg coefficient (A_w).

window of 0.2 to 3.0 V. According to the voltage profiles, the main capacity of both composites is situated between 0.5 and 1.5 V. The initial charge and discharge specific capacities of HC-LVO/C/G composite are about 436 and 712 mAh g⁻¹, which are higher than the values of LVO/C composite (314 and 462 mAh g⁻¹, respectively). But the initial coulombic efficiency (CE) of HC-LVO/C/G composite (61.2%) is slightly lower than that of LVO/C composite (67.9%) due to the more irreversible reactions on the surface of rGO [37,40,41]. The reversible capacity of HC-LVO/C/G composite can be retained at 387 mAh g⁻¹ after 200 cycles (Fig. 6c), which is much higher than that of LVO/C composite (305 mAh g⁻¹). Owing to the introduction of carbon materials, the CE of both composites can remain above 99% since the 10th cycle.

Rate performance of the HC-LVO/C/G and LVO/C composites is also investigated (Fig. 6d). It is clear that the HC-LVO/C/G composite exhibits much improved rate performance than the LVO/C composite. The HC-LVO/C/G composite can deliver an average charge capacity of 428, 403, 366, 337, 244 and 113 mAh g⁻¹, respectively, as the current density is increased stepwise from 0.5 to 1, 5, 10, 20 and 50 C. It is noteworthy that even at a super high current density of 100 C, a stable capacity of 80 mAh g⁻¹ can still be achieved. However for the LVO/C composite, it can only deliver an average charge capacity of 319, 271, 164, 102, 46 and 17 mAh g⁻¹ at the current density of 0.5, 1, 5, 10, 20 and 50 C, respectively. When the current density increases to 100 C, its capacity almost decreases to zero.

For the practical large-scale LIB application, electrode materials are also required to operate at the high current density and possess a long cycle life [42,43]. The HC-LVO/C/G and LVO/C composites electrodes are activated at 1 C for the first 5 cycles and then cycled at 10 C for all the subsequent cycles. As shown in Fig. 6e, the HC-LVO/C/G composite can exhibit the exceptional specific capacity of 312 mAh g⁻¹ even after 1000 cycles at the high current density of 10 C. However, at the same conditions, the LVO/C composite can only deliver the much lower capacity of 121 mAh g⁻¹ after 1000 cycles.

The superior rate capability of the HC-LVO/C/G composite should be derived from the enhanced electrode kinetics which could be clearly evaluated by the EIS tests. Each Nyquist plot is consist of two overlapped semicircles and one straight line (Fig. 7a). Both spectra are fitted by using the equivalent circuit (inset of Fig. 7a). In this equivalent circuit, R_{ele} is the electrolyte resistance, CPE1 and R_{sei} are the capacitance and resistance of the SEI film, respectively. CPE2 and R_{ct} represent the double-layer capacitance and charge-transfer resistance, respectively [43–45]. Furthermore, W_o represents the Warburg impedance. As shown in Tabel 2, R_{sei} and R_{ct} of the HC-LVO/C/G composite are smaller than that of the LVO/C composite apparently. The enhanced electronic/ ionic transport may be attributed from the specific morphology and higher carbon content (especially the extra introduction of rGO) of the HC-LVO/C/G composite.

Diffusion rate of Li⁺ ions into the bulk materials is another important factor to the electrode kinetics. The apparent Li⁺ ions diffusion coefficient (D_{Li^+}) can be calculated from the Warburg region according to Eq. (1) [10,46,47]:

$$D_{Li^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_0^2 A_w^2} \tag{1}$$

where *R* is the gas constant, *T* is the absolute temperature, *A* is the active surface of the electrode (1.12 cm^2), *n* is the total number of electrons transferred in the reaction, *F* is the Faraday's constant, *C*₀ is the molar concentration of Li⁺ ions in the LVO, and *A*_w is the Warburg coefficient. The value of *A*_w was empirically determined from the slope of *Z'* versus $\omega^{-1/2}$ (Fig. 7b) according to Eq. (2):

$$Z' = R_D + R_L + A_w \omega^{-1/2} \tag{2}$$

As shown in Table 2, it is evident that D_{LI^+} of the HC-LVO/C/G composite (4.85 × 10⁻¹⁵ cm² s⁻¹) is several times higher than that of the LVO/C composite (1.21 × 10⁻¹⁵ cm² s⁻¹). These results indicate that the HC-LVO/C/G composite could ensure much easier charge transfer and much faster Li⁺ ions diffusion at the interface of electrode and electrolyte, which lead to the enhanced electrode kinetics.

In order to verify the practical application of the HC-LVO/C/G composite, the HC-LVO/C/G electrode was assembled to full cell with LiCoO₂ (LCO) electrode as the cathode. As shown in Fig. 8, the LCO-HC-LVO/C/G full cell gives rise to an operating voltage of around 3.0 V. A high reversible capacity of 326 mAh g^{-1} can be maintained after 200 cycles at 1 C. The honeycomb structure is strong enough to survive the pressure which is applied when the full cell is assembled (Fig. S2).

Table 2						
R_{sei} , R_{ct} , A_w and D_{Li^+}	of the	HC-LVO/C/G	and	LVO/C	composites	electrodes.

Sample	$R_{sei}(\Omega)$	$R_{ct}(\Omega)$	$A_w \left(\Omega \mathrm{s}^{-1/2} ight)$	D_{Li^+} (cm ² s ⁻¹)
HC-LVO/C/G	13.16	24.11	61.5	$\begin{array}{c} 4.85 \times 10^{-15} \\ 1.21 \times 10^{-15} \end{array}$
LVO/C	17.26	58.48	123.2	



Fig. 8. (a) Cyclic performance and (b) typical discharge-charge curves for the LCO-HC-LVO/C/G full cell at 1 C with capacity limited by anode cycled between 1.5 and 4.2 V (the loading mass of HC-LVO/C/G composite and LCO was about 0.72 and 3.22 mg cm⁻², respectively.).

4. Conclusions

Li₃VO₄/C/rGO (HC-LVO/C/G) ternary composite with honeycomb-like structure has been successfully prepared by a facile onepot spray drying method and followed by heat treatment. This specific honeycomb-like structure can shorten the Li⁺ ions diffusion distance and provide enough space to accommodate the volume change during cycling. Meanwhile, the double coating layer of amorphous carbon and rGO on the surface of Li₃VO₄ nanocrystals can offer enhanced electronic conductivity. Owing to the simultaneous improvement of electrode kinetics and structural stability, the resultant HC-LVO/C/G composite demonstrates impressive high-rate performance and long cycle-life (the high capacity of 312 mAh g⁻¹ can be retained after 1000 cycles at the high current density of 10 C). The superior electrochemical performance suggests that the HC-LVO/C/G composite can be a promising anode material for large-scale LIBs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2017.06.108.

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