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Solvothermal synthesis of Li_3VO_4 : morphology control and electrochemical performance as anode for lithium-ion batteries

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Abstract

In this work, morphology controllable orthorhombic Li_3VO_4 has been synthesized by tuning the solvent composition (volume ratios of ethanol to deionized water) in a solvothermal approach. The resulting Li_3VO_4 samples with various morphologies (coral-shaped particle, self-assembled hierarchical microsphere, cube-like particle, sheet-like structure) show different electrochemical performances when employed as anodes for Li-ion battery applications. The Li_3VO_4 with the self-assembled hierarchical microsphere morphology (volume ratio of ethanol to deionized water at 15:15) exhibits the best electrochemical performance. Furthermore, the subsequent carbon coating process on the microsphere sample has significantly improved the capacities at both low (350 to 430 mAh g^{-1} at 100 mA g^{-1}) and high current (180 to 350 mAh g^{-1} at 2 A g^{-1}) conditions with excellent cycling stability as well.

Highlights

- Morphology controllable orthorhombic Li_3VO_4 is prepared by a solvothermal method (mixture of ethanol and deionized water).
- Different morphologies of Li_3VO_4 (coral-shaped particles, self-assembled hierarchical microsphere, cube-like particle, sheet-like particle) greatly influence the corresponding electrochemical performance.

- The Li_3VO_4 with the self-assembled hierarchical microsphere morphology (the volume ratio of ethanol and deionized water at 15-15) shows the best performance.
- The following carbon coating on self-assembled hierarchical microsphere sample significantly improved the capacity and cycling stability.

Introduction

Lithium-ion batteries (LIBs) are considered as promising energy storage devices for various applications ranging from portable consumer electronics to electric vehicles because of the high energy density and decent power capability [1, 2]. However, the current commercial graphitic anode has a relatively low specific capacity (372 mAh g^{-1}) and a low voltage plateau ($< 0.1 \text{ V vs. Li}^+/\text{Li}$); the low voltage could cause Li-plating upon operation at high current, which is one major setback for graphitic materials. Therefore, intense research is on to find a better alternative to graphite. Conversion and alloy type materials are well-known alternatives because of their high specific capacities [3-5]. However, conversion type materials exhibit large voltage hysteresis, volume variation, relatively higher redox potential and poor cycling stability [6, 7]. Alloy type materials suffer from huge volume change during charging/discharging process and poor cyclability; for instance, Si has a volume change of more than 300% during cycling [8, 9], which generates high mechanical stress that eventually cause the active material to detach from the current collector, leading to the drastic capacity fading [10]. Thus, intercalation type materials are still ideal candidates owing to the negligible volume change, which ensures structural integrity, good reversibility, and high coulombic efficiency of the electrode. Besides graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is another intercalation type material known for its low volume change and high reversibility. However, the high insertion potential (about $1.5 \text{ V vs. Li}^+/\text{Li}$) and low capacity ($\sim 150 \text{ mAh g}^{-1}$) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ restrict its application [11-13].

Recently, Li_3VO_4 (denoted as LVO) anode with β -polymorph has been reported as a promising insertion type material to replace graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It can accommodate up to two mole of Li, corresponding to a theoretical capacity of 395 mAh g^{-1} , which is higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [14]. Besides its high capacity, LVO also has an appropriate voltage window ($0.5\text{--}0.8 \text{ V vs. Li}^+/\text{Li}$), which avoids the safety issue associated with the formation of Li dendrites and guarantees high voltage of the full cell [15, 16]. Thus, these advantages make LVO a promising anode material among the currently studied materials and extensive research has been conducted

on this material [16-21]. To obtain the electrochemical performance of LVO, it is widely accepted that controlling the morphology (i.e. particle size, shape, and dimensionality of LVO) can be feasible. For instance, Li *et al.* prepared a hollow shell-controlled LVO *via* a self-template method, where the thickness of LVO shell can be controlled by adjusting the volume ratio of water and ethylene glycol. The thickness of the shell could affect the final electrochemical activity [22]. Recently, Tartaj *et al.* reported an aerosol spray approach to produce LVO colloidal aggregates with different morphology (spheres and platelet-like) using different reactants, where the spheres outperforms the platelets in terms of electrochemical capabilities [19]. This clearly suggests that the electrochemical response of LVO is strongly dependent on morphology. Therefore, morphology control is very important to achieve high performance.

Apart from the controlling the morphology, improving the electronic conductivity of LVO is another approach of improving electrochemical performance [23-25]. Many methods like wrapping with graphene nanosheets and coating with conductive Ni have been proven effective in improving the electrochemical performance of LVO [23-28]; however, these methods are difficult to realize when it comes to reality. Conventional carbon coating is still one of the most widely used methods because of its low cost and high effectiveness [29].

In the present work, we report a facile solvothermal approach to yield LVO using mixed solvents of deionized water (DIW) and absolute ethanol (EtOH). The morphology of LVO greatly changes while tuning the volume ratio of EtOH/DIW. Coral-shaped particle, self-assembled hierarchical microsphere, cube-like particle, sheet-like structure are obtained when the volume ratios of EtOH to DIW range from 30:0, 20:10, 15:15, 10:20 to 0:30. The Li-storage properties are studied in half-cell assembly and the sample with self-assembled hierarchical microsphere (volume ratio of EtOH to DIW water at 15-15) demonstrates the best performance. The structural characteristics and morphology of the carbon coated and carbon free 15-15 samples were characterized using XRD, field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The electrochemical performance between the carbon free 15-15 and carbon coated 15-15 in the potential range of 0.1–3.0 V was also systematically investigated and described in detail.

Experimental section

Synthesis of Li_3VO_4

First, 2 mmol NH_4VO_3 and 6 mmol $\text{LiOH}\cdot\text{H}_2\text{O}$ were dissolved in 15 mL DIW, and continuously stirred until a homogeneous solution was obtained. Then, 15 mL EtOH was then added to the above transparent solution followed by transferring it to a 45 ml Teflon lined autoclave and maintained for 4 h at 180 °C. Finally, the obtained product was centrifuged and washed 4 times with methanol to form Li_3VO_4 powder, which was dried in vacuum at 80 °C overnight. To investigate the morphology changes with varying volume ratio of solvent components, LVO was prepared with the volume ratio of EtOH and DIW from 30:0, 20:10, 15:15, 10:20, and 0:30 (denoted as 30-0, 20-10, 15-15, 10-20, and 0-30, respectively). The total volume of solvent is 30 mL. For the carbon coating process on 15-15, 100 mg LVO powder was added to 2 mL of a poly(vinylpyrrolidone) (PVP molecular weight 29 K) in EtOH solution (25 mg/mL). This slurry was then stirred until it became dry. The resulting powder was heated at 500 °C for 2 h in Ar atmosphere to form the carbon-based amorphous coating over the surface of LVO particles. It is worth mentioning that methanol was used instead of water to wash LVO since LVO is soluble in water.

Materials characterization

The crystal structure and microstructures were examined by powder X-ray diffraction (XRD, Bruker D8 with Cu $K\alpha$ radiation), SEM, JEOL JSM-7600, Japan and high-resolution Transmission electron microscopy (HR-TEM, JEOL JEM-2100F) at the electron beam energy of 200 kV, respectively. Raman spectra was obtained with a WITecCRM200 Raman system (WITec, Germany) with a laser wavelength of 532 nm (2.33 eV). The galvanostatic charge–discharge cycling test was conducted at 25 °C between 0.1 and 3.0 V vs. Li under various current densities with Neware battery testing system (Neware, BTS-5V10mA, China). Cyclic voltammetry (CV) was performed by using an electrochemical workstation (Autolab, PGSTAT302N) with a scan rate of 0.2 mV s^{-1} over 0.1 to 3.0 V vs. Li^+/Li applied to the test cells.

Electrochemical Characterization

All the electrochemical studies of LVO were examined in CR2016 - coin cells. The electrodes were prepared by mixing 70 wt. % active materials, 20 wt. % Super P (Timcal) and 10 wt. %

binder (PVDF Kynar) in N-methyl-pyrrolidinone (NMP, Sigma Aldrich) to form a homogeneous slurry and coated on Cu foil by the doctor blade technique. The electrode was subsequently dried at 60 °C for 2 h and 120 °C for 10 h in vacuum oven before being assembled into a coin cell in an Ar-filled glovebox (MBraun, Germany) with oxygen and water content less than 1 ppm. The mass loading was about 0.8–1 mg cm⁻². Lithium metal was served as a counter and reference electrode in half-cell configuration. Celgard 2400 was used as separator and filled with 1 M solution of LiPF₆ dissolved in ethylene carbonate/diethylene carbonate (EC:DEC = 1:1 by volume, Charslton Technologies Pte. Ltd.) was used as the electrolyte. The specific capacity for carbon-coated composite was calculated based on the total weight including LVO and amorphous carbon.

Results and discussion

Fig. 1 SEM images of Li_3VO_4 at: a) 30-0 (V:Li=2:6 volume ratio of EtOH:DI water=30:0) ; b)20-10 (V:Li=2:6 the volume ratio of EtOH:DIW=20:10); c,d) 15-15 (V:Li=2:6 volume ratio of EtOH:DIW=15:15) at different magnification; e) 10-20 (V:Li=2:6 the volume ratio of

EtOH:DIW=10:20); f) 0-30 (V:Li=2:6 the volume ratio of EtOH:DIW=0:30). The total volume of EtOH and DIW is 30 mL.

The morphologies of as-synthesized LVO samples at various EtOH/DI water ratio of 30:0, 20:10, 15:15, 10:20 and 0:30 were examined using FE-SEM with the results shown in Fig. 1. As can be seen, when 30 mL ethanol is used as solvent without DIW, spherical particles with size around 1 μm are formed (Fig. 1a). The obtained particles appear coral-like rods with the addition of EtOH/DIW at volume ratio of 20:10 (Fig. 1b). Self-assembled hierarchical microspheres, consisting of many small primary particles, are produced when the EtOH/DIW ratio is reduced to 15:15 (Fig. c and d). Lowing EtOH/DIW ratio down to 10:20 results in the formation of cubic-like LVO particles with the size of around 4 μm (Fig. 1e). LVO particles become super large with sheet-like structure when the EtOH/DIW ratio is further reduced to 0:30 (Fig. 1f). Apparently, the particle size increases with the increase of the content of DIW except the first sample. Since the first sample was prepared using 30 ml EtOH as solvent, the phase is not pure. Further discussion of this is carried out in the XRD section. Meanwhile, it is proved that there are several morphologies of LVO and is dependent on the solvent and volume ratio. The different volume ratio of the solvents provides different polarities and saturated vapor pressures, which enables the formation of these diverse morphologies. The amount of individual nucleus formation, the amalgamation, and the direction of preferential growth of the nucleus are largely affected by the solvents. Solvents with high degree of supersaturation favor multi-dimensional growth because they are most affected by the polarity and solubility, whilst anisotropic low dimensional growth is favored at low supersaturation [30, 31]. Solvent polarity and metal salts' solubility in solvent are affected by mixing different amount of alcohol and water as solvent. This is proved **by the fact** that the bulk LVO can be produced in pure DIW.

Fig. 2 XRD patterns of the LVO particles synthesized at 0-30, 10-20, 15-15, 20-10 and 30-0 (the volume ratio of EtOH and deionized water (DIW)).

Fig. 2 shows the XRD patterns of LVO prepared at different EtOH/DIW ratios. The reaction temperature and time are set at 180 °C and 4 h, respectively. Samples prepared at EtOH/DIW volume ratios of 20:10, 15:15, 10:20, and 0:30 are identified to be pure phase LVO, and all the sharp reflections in XRD patterns are generated from Li_3VO_4 orthorhombic phase with lattice constants $a = 6.319 \text{ \AA}$, $b = 5.448 \text{ \AA}$, and $c = 4.940 \text{ \AA}$ (JCPDS NO. 38-1247). However, secondary phase of LiVO_3 presents when the ratio of EtOH/DIW is 30:0. This may be due to NH_4VO_3 that does not fully dissolved in absolute ethanol even at 180 °C. With the increase of ethanol content, the intensity of overall peaks is depressed, indicating the reduction of crystallinity.

Since LVO is soluble in DIW (seen Fig. S1), methanol was used to wash away the excess LiOH. It is worth noting that LiOH has a much higher solubility (9.76 g/100 g > 2.36 g/100 g) in methanol than in ethanol. The morphology after washing with DIW and methanol was imaged in an SEM and is shown in Fig. S1 c and d, where 4 μm -sized particles are etched and appear as flake-like shapes within only 1 min of washing period followed by sonication of 1 min. The dissolution of LVO in DIW has been also reported previously [22, 25].

Fig. 3 (a) First three CV cycles of 15-15; (b) Galvanostatic discharge–charge profiles of 15-15 and 30-0 for the first four cycles at a current rate of 0.1 A g⁻¹ in the voltage range of 0.1–3.0 V vs. Li⁺/Li; (c) Rate performance of 0-30, 10-20, 15-15, 20-10 and 30-0 (the volume ratio of EtOH and DIW) at varying current densities from 0.1 to 4 A g⁻¹ in the voltage range of 0.1–3.0 V vs. Li⁺/Li; (d) Cycling performance of 0-30, 10-20, 15-15, 20-10 and 30-0 at 100 mA g⁻¹.

The lithium storage performance of samples as anode materials for LIBs was evaluated by half-cells. Cyclic voltammetry (CV) of the EtOH/DIW ratio of 15-15 for the first three cycles was performed at a scan rate of 0.2 mV s^{-1} in the voltage range of 0.1–3 V, as shown in Fig. 3a. Fig. S2 shows the CVs of other samples with the different EtOH/DIW ratios, i.e. 0-30, 10-20, 20-10, and 30-0. The 1st cycle is apparently different from the subsequent two cycles for the all 5 samples, which is usually ascribed to the occurrence of side reaction on the electrode surfaces and interfaces and the formation of SEI (solid electrolyte interface) film. The two reduction peaks around 0.87 V and 0.54 V after first cycle are attributed to the insertion of lithium ions to Li_3VO_4 . As a result, V^{5+} is reduced to V^{3+} [15, 32]. In addition, the broader oxidation peak around 1.35 V in all cycles is related to the desertion of lithium ions from Li_3VO_4 , i.e. the oxidation of V^{3+} to V^{5+} . It is noteworthy that the oxidation peaks from the first to third cycles almost overlap, indicating the high reversibility. More importantly, both samples with the EtOH/DIW ratios of 15-15 and 30-0 have a current that is about 10 times higher than that of the samples with EtOH/DIW ratios of the 10-20 and 0-30. The cathodic peak at around 1.5 V is related to conductive carbon Super P, which can be observed in Fig. S1f, where the CV of Super P is scanned. Fig. 3b shows the typical galvanostatic discharge–charge curves of two samples with EtOH/DIW ratios of 15-15 and 30-0 at a current density of 100 mA g^{-1} between 3.0 to 0.2 V. The sample with the EtOH/DIW ratio of 15-15 has a higher capacity and a relatively longer plateau from the 2nd cycle onwards than the sample with the EtOH/DIW ratio of 30-0, which is consistent with the CV measurements.

The rate performance of 0-30, 10-20, 15-15, 20-10 and 30-0 samples were evaluated by charge–discharge at various current densities from 100 to 4000 mA g^{-1} (Fig. 3C). With the increase of current density, the capacity drops due to the higher polarization and the electrochemical reaction performed only by the surface of the active material. In comparison, 15-15 exhibits the best performance among all the samples prepared from volume ratio of EtOH and DIW. This result is consistent with the CVs results (Fig. 3a) and cycling performance in Fig. 3d. It is noted that the capacity is restored to the initial value when the current density is abruptly reduced to 100 mA g^{-1} after the high current discharge–charge measurements, indicating high reversibility. Cycling performance is another critical factor for anode materials in the practical applications. Fig. 3d shows the cycling performance at a moderate current density of 100 mA g^{-1}

for 100 cycles. Sample 15-15 shows the highest capacity and stability among all the samples tested.

Fig. 4 TEM images confirm the carbon coating. (a and b) TEM and HR-TEM images of the pristine 15-15 before carbon coating; (c and d) TEM and HR-TEM images of the carbon coated 15-15 (C 15-15).

To improve the performance of 15-15, carbon coating process was conducted using PVP as carbon source and EtOH as solvent. From Fig. 4a and 4c, the low magnification TEM images

of both 15-15 and C 15-15 demonstrate that the microsphere particles are clustered as a number of small particles. HR-TEM images (Fig. 4b and 4d) indicated that the microspheres are polycrystalline clearly covered by amorphous carbon (Fig. 4d).

Fig. 5 (a) XRD patterns for coated and uncoated 15-15; (b) Raman spectra of the coated and carbon free 15-15.

Fig. 5a shows the XRD patterns for 15-15 before and after carbon coating. Fig. 5b is the Raman spectrum of the products, which shows a weak peak at 824 cm^{-1} associated with the vibration of Li_3VO_4 crystal lattice and two strong peaks at 1358 and 1601 cm^{-1} that correspond to the disorder (D-band) and graphitic (C-band) phases of carbon, respectively [33]. These results indicate that $\text{Li}_3\text{VO}_4/\text{C}$ composite architectures were successfully synthesized. Thermal analysis was employed to study the composition of the C 15-15 in air. Fig. S3 shows the TG of the C-coated 15-15. The weight loss below 200°C can be ascribed to the elimination of absorbed waters, and the weight in temperature region $200\text{--}800^\circ\text{C}$ corresponds to the burning of carbon. Thus, the weight of carbon can be estimated to be 14 wt. % in the C 15-15.

Fig. 6 (a) First three CV cycles of carbon coated 15-15 (C 15-15); (b) Rate performance of 15-15 and C 15-15 at varied current densities from 0.1 to 4 A g⁻¹ in the voltage range of 0.1–3.0 V vs Li⁺/Li; (c) Cycling performance of C 15-15 and 15-15 at 2 and 4 A g⁻¹; (d) Cycling performance of 15-15 and C 15-15 at 100 mA g⁻¹.

The electrochemical performance of 15-15 and carbon coated 15-15 are further investigated. Fig. 6a shows the CV curves of C 15-15, where a main reduction peak is visible at about 0.5 V and two oxidation peaks at about 1.07 and 1.35 V. The 1.07 V oxidation peak disappears after the 1st cycles, which is similar to previous reports [15, 34]. The almost overlapping 2nd and 3rd CV cycles indicates good cycling stability. Additionally, C 15-15 has a slightly higher current density on the CV curves, which was verified by EIS measurements. The impedance of the C 15-15 and 15-15 electrodes after 3 CV cycles were evaluated and the typical Nyquist plots are displayed in Fig. S4. The EIS spectra consists of a medium-to-high-frequency

compressed semicircle, describing the charge transfer resistance (R_{ct}) and a low-frequency tail corresponding to the Warburg impedance related to the Li^+ ions diffusion within the particles. As clearly seen, C 15-15 has a semicircle with smaller diameter compared to that of 15-15, indicating the lower R_{ct} for C 15-15 electrode. The rate performance is also evaluated and the capacities are measured to be 430, 420, 400, 380, 324, and 250 mAh g^{-1} at rates of 100, 200, 400, 800, 2000, and 4000 mA g^{-1} , respectively (Fig. 6b). When the current density finally returns to 100 mA g^{-1} , the charge capacity recovers to 430 mAh g^{-1} , indicating the excellent rate capability of the C 15-15. Compared with the 15-15, C 15-15 shows higher capacities at various rates. Moreover, for C 15-15, at the current densities of 100 mA g^{-1} , discharge capacity of 430 mAh g^{-1} is maintained after 100 cycles, higher than 350 mAh g^{-1} of bare 15-15 (Fig. 6d). Even at a higher current density of 2 A g^{-1} , the C 15-15 electrode delivers a capacity as high as 350 mA g^{-1} , which is much higher than 180 mAh g^{-1} of 15-15 at the same current density of 2 A g^{-1} . In addition, when a current density of 4 A g^{-1} is used, C 15-15 still can have a capacity of 230 mAh g^{-1} even after 500 cycles. This result supports the fact that carbon coated 15-15 could successfully enhance electronic/ionic transport within the anode, thus resulting in improved electrochemical kinetics.

Conclusion

In summary, Li_3VO_4 samples with different morphologies have been synthesized via a solvothermal method with different volume ratios of EtOH and DIW. Their electrochemical performances as anode materials for LIB were investigated. The sample with EtOH and DIW volume ratio of 15-15 was found to show the best performance among all the samples prepared. In addition, the carbon coating process on 15-15 greatly improves its capacities from 350 to 430 mAh g^{-1} at 100 mA g^{-1} and 180 to 350 mAh g^{-1} at 2 A g^{-1} . These results can be attributed to the formation of conductive carbon coating network on the LVO microsphere surface. These properties make C 15-15 a promising anode material for lithium ion batteries application.

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Supporting Information

for

Solvothermal synthesis of Li_3VO_4 : morphology control and electrochemical performance as anode for lithium-ion batteries

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Fig. S1. SEM images of the as-synthesized LVO (EtOH:DI water 0:30, Li/V=36:2) through solvothermal synthesis and washed with Methanol and DI water: a) As-prepared LVO; b) Washed with methanol for 1 min and sonication for 1 min; c) Washed with DI water for 1 min and sonication for 1 min; d) High magnification of image C.

Fig. S2. First three Cyclic voltammetry (CVs) of LVO: a) 30-0 (LVO prepared from Li:V=2:6, $V_{\text{EtOH}}:V_{\text{water}}=30:0$); b) 20-10 (LVO prepared from Li:V=2:6, $V_{\text{EtOH}}:V_{\text{water}}=20:10$); c) 15-15 (LVO prepared from Li:V=2:6, $V_{\text{EtOH}}:V_{\text{water}}=15:15$); d) 10-20 (LVO prepared from Li:V=2:6, $V_{\text{EtOH}}:V_{\text{water}}=10:20$); e) 0-30 (LVO prepared from Li:V=2:6, $V_{\text{EtOH}}:V_{\text{water}}=0:30$); f) Super P in the first three cycles at a scanning rate of 0.2 mV s^{-1} in the voltage range from 0.1 to 3 V.

Fig. S3. TGA curves of C 15-15(carbon coated Li_3VO_4 at volume ratio of EtOH:DI at 15-15).

Fig. S4. The typical Nyquist plots of C 15-15 and 15-15 after 3 cycles of CV.