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Morphology Controlled Lithium Storage in Li_3VO_4 AnodeGuang Yang,^{†ab} Bowei Zhang,^{†a} Jianyong Feng,^a Zhiqiang Wang,^a Vanchiappan Aravindan,^{ab}Muthiah Aravind,^{ab} Jilei Liu,^{*c} Madhavi Srinivasan,^{*ab} Zexiang Shen^{abc} and Yizhong Huang^{*a}Received 00th January 20xx,
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Li_3VO_4 (LVO) anode materials with controllable morphologies from spherical-assembly, single-crystal nanorods, flower shape, to bulk-shape were designed via solvothermal approach using different alcohols (*i.e.*, ethanol, methanol, propanol, and butanol). XRD, SEM, BET, Raman and FTIR and galvanostatic charge/discharge measurements were carried out to correlate the structure/morphology with their electrochemical characteristics. Experimental results reveal that both structure and morphology play important roles in the Li^+ ion storage of LVO, which degrades in the sequential order from nanorods, sphere, flower to bulk. The LVO nanorods are hierarchical and have a small particle size, high specific surface area, and high crystallinity, thus exhibit the largest Li^+ ion diffusion coefficient and best electrochemical performance among the four electrodes. Moreover, carbon that is coated over single-crystal LVO nanorods further enhances the Li^+ ion storage. It is reasonable that the carbon-coated LVO nanorods deliver a high reversible capacity of 440 mAh g^{-1} at 0.1 A g^{-1} with good cycling stability and demonstrate great practical application. In addition, the results promote better fundamental understanding of the Li^+ ion storage behavior in LVO and provide insight in guiding the optimal design of LVO and other vanadium-based electrode materials.

Introduction

The sharp proliferation of electric automotive and regenerative electric energy storage system (EES) drives the search of high-performance power sources that have high energy density and power density. Stable Li^+ ion intercalation chemistry of graphite ensures the success of LIBs over the past decades. However, challenges facing graphite anode such as limited specific capacity (372 mAh g^{-1}) and safety issue related to Li dendrite formation upon Li^+ ion intercalation at low potential (close to 0 V), especially at high rates, promote urgent demands for novel anode alternatives with both large capacities and more positive intercalation voltages (*vs.* Li^+/Li).^{1–2} Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been exploited since it operates with zero strain, high reversibility, and good rate performance.^{3–7} Nevertheless, its low specific capacity ($\sim 150 \text{ mAh g}^{-1}$) and relatively high operating potential (about 1.5 V *vs.* Li^+/Li) sacrifices the overall cell performance. In addition to insertion

type anodes,^{8,9} conversion-type anodes (*i.e.*, transition metal oxide and metal sulfides etc.),^{10,11} and alloying-type anodes (*e.g.*, Si and Sn-based materials)^{10–12} have been also investigated. The conversion-type anodes generally deliver a specific capacity of 2–3 times of that of graphite. Since the theoretical value is determined by the oxidation state of metal ions.¹³ However, they suffer from poor kinetics, low energy efficiency and large polarization associated with the energy barrier to trigger the cleavage of the metal-oxygen and/or sulfur bonds.¹⁰ The alloying-type anodes can deliver ultra-high capacities, but at the expense of huge volume change and poor cycling performance. Given the improved specific capacity and appropriate intercalation potential, intercalation-type anodes are intrinsically attractive from the perspective of highly reversible Li^+ insertion/extraction and negligible volume change upon cycling.

More recently, Zhou *et al.* reported such a material, $\beta\text{-Li}_3\text{VO}_4$ (LVO), with high reversible capacity (394 mAh g^{-1} , based on $\text{Li}_3\text{VO}_4 + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_{3+x}\text{VO}_4$, $0 \leq x \leq 2$) and suitable Li^+ ion intercalation potential (0.5 V $\sim$ 1.0 V, *vs.* Li^+/Li).¹⁴ The orthorhombic LVO exhibits hollow lantern-like 3D framework consisting of a regular array of corner-shared VO_4 tetrahedra and LiO_4 tetrahedrons, which provides lots of empty sites and intercalation channels for Li^+ ion.¹⁵ Moreover, the high ionic conductivity of LVO ($10^{-4} \sim 10^{-6} \text{ s cm}^{-1}$)^{16,17} ensures fast Li^+ ion diffusion. *Ex-situ* XRD results revealed that the insertion of Li^+ into LVO starts with a solid-solution step and follows with a two-phase reaction.¹⁵ Theoretical calculations also showed

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that the reversible phase transformation from Li_3VO_4 to Li_5VO_4 is energetically favorable (with a biphasic reaction at 0.7 V, vs. Li^+/Li) upon 2 Li insertion/extraction process. Nonetheless, for one more Li insertion, this process is difficult as manifested by the low predicated voltage (0.14 V, vs Li^+/Li) and the major structural rearrangements (20% volume variation).¹⁸ However, experimental results demonstrate the practical feasibility of the third Li insertion although the underlying mechanism is still unclear. For example, a high reversible specific capacity of 540 mAh g^{-1} (about 2.7 Li) was reported for $\text{Li}_3\text{VO}_4/\text{C}$ composite at a current density of 150 mA g^{-1} .¹⁹ The carbon-coated LVO prepared by solid-state method delivers a reversible capacity of 547.1 mAh g^{-1} based on GITT tests and *in-situ* XRD characterizations.¹⁵ Further work has also shown that the synthesis method, crystallinity and the morphology greatly affect the electrochemical properties of electrode materials.²⁰ For example, micro-sized LVO (0.8 - 2.0 μm) prepared by solid-state method delivers the first discharge and charge capacity of 345 and 258 mAh g^{-1} , respectively.²¹ These values rise up to 469 and 326 mAh g^{-1} for hollow cuboid LVO (0.8-2.0 μm) synthesized by a sol-gel method,²² and 624 and 481 mAh g^{-1} for nano-sized LVO (10-100 nm) produced by a hydrothermal method.²³ Despite significant progresses have been made in synthetic optimization,²⁴ morphology tailoring,^{22, 25, 26} surface modification,^{15, 27, 28} and/or electrode hybridization²⁹⁻³³ so far, LVO is still far from practical applications due to the lack of understanding in i) a comprehensive relationship between materials structure properties with electrochemical characteristics, and ii) the fundamental electrochemistry.

Herein, we synthesized a series of LVO with controlled morphologies from spherical-assembly, single-crystal nanorods, flower shape, to bulk by a solvothermal approach using different alcohols. To investigate the morphology effect on the anodes, XRD, SEM, FITR, Raman CV and galvanostatic charge/discharge were employed to examine their physical properties with electrochemical characteristics. The results reveal that single-crystal LVO nanorods show the best performance in terms of rate performance and cyclability. This enhanced electrochemical performance can be ascribed to i) the high surface area of the porous rod-shaped structure that offers favorable ion diffusion and electron transfer, and ii) the small particle size that reduces the diffusion length. Moreover, further improvement in the electrochemical performance was achieved using carbon coating on the single-crystal LVO nanorods. The as-prepared LVO/C delivers a high reversible capacity of 430 mA g^{-1} at a current of 100 mA g^{-1} , along with good rate performance and cycling stability.

Experimental procedures

Material synthesis

Single-crystal Li_3VO_4 nanorods (denoted as LVO-ROD): 0.234 g NH_4VO_3 and 0.245 g LiOH monohydrate were mixed in 10 mL DI water first, and then stirred until the chemical fully dissolved. After that, 20 mL ethanol was added to the above transparent solution. Subsequently, the above solution was

transferred to a 45 mL autoclave and heated at 180 °C for 4 hrs. Finally, the obtained product was centrifuged and washed four times with methanol, which was then dried at 80 °C in vacuum overnight.

Spherical-assembly shaped, large single-crystal flower structure and bulk-shape Li_3VO_4 (denoted as LVO-SPHERE, LVO-FLOWER, and LVO-BULK): these Li_3VO_4 structures were obtained by simply replacing ethanol with other alcohols (Methanol, Propanol, and Butanol). For the carbon coating process on LVO-ROD, 200 mg LVO-ROD powder was added to 4 mL of a poly(vinylpyrrolidone) (PVP Molecular Weight 29K) / EtOH solution (25 mg/mL). This slurry was then ground until dry. The resulting powder was heated at 500 °C for 2 h in Ar atmosphere to pyrolyze PVP forming a carbon-based amorphous coating. It is noteworthy that methanol instead of water was used to wash LVO because LVO is soluble in water.

Materials Characterization

The powder X-ray diffraction patterns were collected in Bruker D8 Advance using $\text{Cu K}\alpha$ radiation. The morphologies of synthesized samples were characterized using scanning electron microscopy (SEM, JEOL JSM-7600, Japan) and high-resolution Transmission electron microscopy (HRTEM, JEOL JEM-2100F). Raman spectra were obtained using a WITecCRM200 Raman system (WITec, Germany).

Electrochemical Characterization

The electrochemical performance of LVO was evaluated by assembling 2016 coin cells in an argon-filled glovebox (MBraun, Germany) with oxygen and water content less than 1 ppm. The electrodes were prepared by mixing 70 wt. % active materials, 10 wt. % binder (PVDF Kynar), and 20 wt. % Super P (Timcal) in a weight ratio of 7:1:2 in N-methyl-pyrrolidinone (NMP, Sigma Aldrich). The typical electrode was dried at 60 °C for 2 h and 120 °C for 10 h in a vacuum oven before being assembled into a coin cell in the glovebox. The mass loading was about 1 mg cm^{-2} . Lithium foil served as a counter electrode and Celgard 2400 was used as the separator. The electrolyte was composed of 1 M solution of LiPF_6 dissolved in ethylene carbonate/diethylene carbonate (EC: DEC = 1:1 by volume, Charslton Technologies Pte. Ltd.). The specific capacity for Carbon coated LVO-ROD sample is calculated based on the total weight of LVO and amorphous carbon. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed using Solartron Instrument. The frequency of EIS measurement was carried out from 100 KHz to 0.01 Hz with an AC signal of 10 mV amplitude.

Results and discussion

LVO with different morphologies (Fig. 1a-d & Fig. S1) was synthesized in Methanol, Ethanol, Propanol, and Butanol solvothermal solvents. Spherical shape, nanorod shape, flower-like shape and bulky LVO were obtained. In the text below, these products are simply illustrated as LVO-SPHERE, LVO-ROD, LVO-FLOWER, and LVO-BULK, respectively. LVO-SPHERE is a microspherical-assembled cluster (Fig. 1a). LVO-

Fig. 1 Morphology and Structure. SEM images of: (a) LVO-SPHERE; (b) LVO-ROD; (c) LVO-FLOWER; (d) LVO-BULK; all the SEM images show the same magnification. (e) XRD patterns, (f) Raman and (g) FTIR spectra. (h) TEM image and (i) HRTEM image of LVO-ROD, the inset shows the corresponding FFT image.

ROD shows hierarchical structure consisting of rods with diameter range from 50-100 nm (Fig. 1b and S3). Flower-shape LVO compose of primary particles with the size around 1 μm (Fig. 1c), whilst LVO-BULK appears large crystals with the size around 7 μm (Fig. 1d). Table 1 lists all these products along with their corresponding particle sizes. Powder-XRD results reveal that all samples are a pure phase and determined to be LVO phase (JCPDS NO. 38-1247) (Fig. 1e). LVO-ROD shows the broadest peak in the XRD pattern indicating the smallest crystallite size, in good agreement with the SEM result. The Rietveld refined XRD patterns of the samples are shown in Fig. S2. The refined crystallographic parameters are presented in Table S1. The lattice volume of LVO-ROD is largest among all these samples and this allows the fastest diffuse of Li ions leading to the highest Li ion diffusion coefficient. Raman and Fourier transform infrared (FTIR) spectroscopies were used to further investigate the structural features of the samples. In Fig. 1f, the peak at 819 cm^{-1} is attributed to symmetric stretching of VO_4^{3-} , whereas the peak at 791 and 785 is assigned to asymmetric stretching of VO_4^{3-} . The peak at 328 cm^{-1} is generated by the VO_4 vibration. Almost identical spectra collected from all the samples indicate that no impurity phases are present.^{26, 34, 35} Fig. 1g shows the FTIR spectra of the samples and the assignment of these peaks are summarized in Table S2. Both peaks at 3433 and 1637 cm^{-1} are attributed to the moisture inside the samples. The peak at around 1420 cm^{-1} is associated with the amorphous carbon, which may come from the synthesis process using alcohol as solvents.³¹ Another small peak at around 2344 cm^{-1} is related to the adsorption of CO_2 on the sample surface.³⁶ The main peaks located at 851, 806 and 466 are assigned to the symmetric, asymmetric stretching of V-O, and symmetric stretching of V-O-V, respectively.^{37, 38} The peak around 851 cm^{-1} is different for all the four samples, which is due to the different particle sizes as well as the different preferred crystallographic orientation formation under different

preparation conditions as described in XRD section.³⁹⁻⁴¹ Fig. 1h shows a representative TEM image of a single nanorod. Uniform lattice fringes have been identified from SAED pattern in Fig. 1i. The lattice fringes are measured to be 0.41 nm, which correspond to the d-spacing of the (110) plane of Li_3VO_4 . Moreover, the distinct periodic dots in SAED patterns (Fig. 1i and Fig. S3) suggest its single-crystal feature. HRTEM image and the corresponding fast-Fourier transform (FFT) from another rod also demonstrate that the rods are single crystal (Fig. S3d-e). The TEM image and the corresponding EDX elemental mapping images of V and O (Fig. S3f-i) indicate the presence and uniform distribution of element V and O across the nanorod.

The electrochemical performance of LVO-SPHERE, LVO-ROD, LVO-FLOWER, and LVO-BULK were investigated and compared. Typical cyclic voltammetry (CVs) curves of LVO-ROD for the first three cycles are illustrated in Fig. 2a. The reduction peak at around 0.28 V in the first cathodic scan is resulted by the SEI (solid electrolyte interface) formation and/or side reactions. A small reduction peak at around 1.4 V comes from the super P carbon additives (Fig. S4). CV curves overlap well from the 2nd cycle onwards, indicating the good reversibility and cycling stability. Two dominant reduction peaks around 0.87, 0.54 V appear in the subsequent cycles, which are correlated with the multistep insertion of lithium ions to Li_3VO_4 accompanied by the phase change to $\text{Li}_{3+x}\text{VO}_4$.^{11, 15, 42, 43} The oxidation peak around 1.35 V demonstrates the delithiation process with the oxidation

Table 1 LVO samples particle size, BET surface area and pore volume

Sample	Particle size	S_{BET}	Pore
		calculated (m^2/g)	volume (cm^3/g)

LVO-SPHERE	Primary: 100–1000 nm Secondary: 4 μm	1.35	0.004828
LVO-ROD	Dia: 50–100 nm Length: 100–500 nm	10.49	0.059163
LVO-FLOWER	Primary: 0.5–1 μm Secondary: 5 μm	0.94	0.003664
LVO-BULK	7 μm	0.05	0.000396

from $\text{Li}_{3-x}\text{VO}_4$ to LVO. Similar redox reactions were also

Fig. 2 Lithium storage behavior. (a) Typical CV cycles of LVO-ROD at a sweep rate of 0.2 mV s^{-1} ; (b) Galvanostatic discharge-charge profiles of LVO-ROD for the first three cycles at a current rate of 0.1 A g^{-1} in the voltage range of $0.1\text{--}3.0 \text{ V vs Li/Li}^+$; (c) Comparative rate performance and (d) cycling performance of LVO-SPHERE, LVO-ROD, LVO-FLOWER and LVO-BULK. (e) EIS spectra collected after 3 cycles of CV scanning; (f) Dependence of oxidation peak current on the square root of scan rate for LVO-SPHERE, LVO-ROD, LVO-FLOWER, LVO-BULK and C@LVO-ROD.

identified for LVO-SPHERE, LVO-FLOWER, and LVO-BULK (Fig. S4). GDC profiles (Fig. 2b) in the first cycle deliver three voltage plateaus at 1.4 V , 0.75 V and 0.6 V , which correspond to the irreversible reactions but are not observed in the second cycle, in good agreement with the CV results. The LVO-ROD electrode produces an initial discharge capacity of 550 mAh g^{-1} and first charge capacity of around 370 mAh g^{-1} with the first-cycle coulombic efficiency of 67.28% . The capacity loss is mostly due to the irreversible reactions including the decomposition of electrolyte and the formation of the SEI film, as identified from the shape difference between the discharge profiles of the first and second cycles. The electrochemical performance of LVO-ROD is superior over that of LVO-SPHERE, LVO-FLOWER and LVO-BULK, probably due to its large surface area and high electron transportation. More discussion will be given later (Fig. S5). Moreover, the LVO-ROD exhibits enhanced rate performance compared with other LVO samples (Fig. 2c). For example, a discharge capacity of 150 mAh g^{-1} can

be achieved even at a high current density of 4000 mA g^{-1} . Particularly, a high capacity of 280 mAh g^{-1} can be still produced when the current density reduces back to 100 mA g^{-1} . Such excellent cycling performance is also well illustrated in Fig. 1d, in which the LVO-based electrodes shows a trivial decrease in specific capacities upon cycling. A capacity of 250 mAh g^{-1} (at 100 mA g^{-1}) is retained till 100 cycles for LVO-ROD, with a capacity retention of 72% . The LVO-SPHERE, LVO-FLOWER and LVO-BULK deliver smaller specific capacities but shows reasonable cycling

Table 2 Equivalent circuit parameters and apparent Li ion diffusion coefficient calculated from CV rates

Sample	$R_1 (\Omega)$	$R_f (\Omega)$	$R_{ct} (\Omega)$	$D_{\text{Li}^+} (\text{cm}^2 \text{ s}^{-1})$
LVO-SPHERE	2.5	5.1	340	2.622×10^{-12}
LVO-ROD	2.4 (100th cyc)	4.6 (100th cyc)	76 (100th cyc)	3.722×10^{-12}
LVO-FLOWER	2.6	7.8	350	4.114×10^{-13}
LVO-BULK	2.3	10.2	260	1.084×10^{-12}
C@LVO-ROD	2.7 (100th cyc)	10.1 (100th cyc)	110 (100th cyc)	4.815×10^{-11}

stability, suggesting that LVO is a promising anode for LIBs. The improved electrochemical performance in LVO-ROD is attributed to its unique structure. Firstly, it has the smallest particle size that reduces the Li-ion diffusion length (Table 1). As seen in Fig. S6, the particle size of single-crystal LVO-ROD is about $50\text{--}100 \text{ nm}$ in diameter and $100\text{--}500 \text{ nm}$ in length, which are all less than the dimensions of flower-shaped LVO-FLOWER ($0.5\text{--}1 \mu\text{m}$ for primary particle size) and bulk-shaped LVO-BULK ($\sim 7 \mu\text{m}$). Secondly, it is porous and provides the largest specific surface area that facilitates electrolyte diffusion. BET results (Fig. S7 & Table 1) reveal that the specific surface area decrease in the sequential order of LVO-ROD > LVO-SPHERE > LVO-FLOWER > LVO-BULK, which is consistent with the trend of electrochemical performance. In addition, both LVO-SPHERE and LVO-ROD possess mesopores with the pore size distribution around 40 nm . LVO-ROD has the highest pore volume among the samples (Fig. S7 and Table 1). LVO-SPHERE has a spherical-assembly structure. The relatively lower capacity compared to LVO-ROD probably due to its structure being less porous than LVO-ROD. In contrast, LVO-FLOWER has a wide pore size distribution from 50 and 120 nm . All these factors allow the electrochemical performance of LVO-ROD above others.

EIS measurements and CV testing were carried out to shed more light on the kinetic properties of various LVO-based electrodes. In Fig. 2e, each EIS curve consists of a semicircle and an inclined line. R_1 in high frequency can be assigned to electrolyte resistance. While each semicircle comprises two compressed semicircles: resistance of SEI film (R_f) in the high frequency, and resistance of charge-transfer (R_{ct}) in the middle

frequency.^{22, 44} The Warburg impedance in low frequency is related to Li ion diffusion within the particles. Based on the fitted results from equivalent circuit model, the R_{ct} of LVO-SPHERE, LVO-ROD, LVO-FLOWER, and LVO-BULK are turned out to be 340, 76, 350 and 260 Ω , respectively (Table 2). LVO-ROD exhibits lowest R_{ct} , indicating a fastest charge-transfer process. This is further supported by CV testing under different sweep rates (Fig. S8). The redox peak separation (voltage difference between anodic peak and cathode peak) increases gradually with sweep rate, implying the increasing polarization. The apparent lithium diffusion coefficient in various LVO-based electrodes can be calculated by the classical Randles-Sevchik equation:

$$I_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} C_0 v^{1/2} \quad (1)$$

where I_p is the peak current, A the apparent surface area, D_0 the diffusion coefficient and v the CV scanning rate and C_0 is the maximum Li^+ concentration ($9.8 \times 10^{-3} \text{ mol cm}^{-3}$). Fig. 2f shows the linear relationship between the oxidation peaks I_p and the square root of the scan rate from 0.2 to 0.8 $\text{mV s}^{-1/2}$. The diffusion coefficient is calculated to be $3.722 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for LVO-ROD, which is higher than those of LVO-SPHERE, LVO-FLOWER and LVO-BULK (Table 2). This enhanced kinetic contributes to the better performance of LVO-ROD. To further investigate the effect of different morphologies on the electrochemical performance, the total charge storage at a

certain sweep rate was quantified on the basis of separating the specific contribution from the capacitive and diffusion-controlled charge at a fixed voltage.⁴⁵ The results (Fig. S8f and Fig. S9) reveal that the LVO-ROD exhibits the highest intercalation effects contribution ratio ($\sim 97\%$), probably due to its good crystallinity and enhanced ion diffusion.

To further boost the electrochemical performance of LVO-ROD, carbon coating was conducted by using PVP as a carbon source. The bare LVO-RODs appear in rod-shaped particles (Fig. 3a), and they are aggregated upon high-temperature carbonization process (Fig. 3b). An amorphous carbon layer with non-uniform thickness is observed on the surface of LVO particle (Fig. 3c). The presence of carbon layer is further supported by Raman spectra (Fig. 3d), in which the characteristic D and G band peaks of graphite are clearly detected, in addition to the peaks that are related to LVO-ROD. Element mappings show the homogenous distribution of carbon on LVO, forming C@LVO-ROD composites (Fig. 3g-j). Thermal analysis was carried out to determine the content of the C@LVO-ROD (Fig. 3e). The weight loss below 200 $^{\circ}\text{C}$ is attributed to the elimination of absorbed water, and the weight loss in temperature region 200 – 800 $^{\circ}\text{C}$ is associated with the escape of carbon. The weight of carbon was therefore estimated to be 6.5 wt. % in the C@LVO-ROD. These particles are identified as orthorhombic Li_3VO_4 , on the basis of fast-Fourier transform (FFT) analysis (inset of the Fig. 3c). The

Fig. 3 Carbon coating characterization. (a, b) TEM images of LVO-ROD and C@LVO-ROD, (c) HRTEM images of the carbon coated LVO-ROD (C@LVO-ROD), Inset: FFT image of C@LVO-ROD; (d) Raman spectra of the LVO-ROD and C@LVO-ROD, (e) TGA curves of C@LVO-ROD; (f) XRD patterns for LVO-ROD and C@LVO-ROD; (g, h, i, j) SEM image and elemental mapping images of V, O and C for C@LVO-ROD and inset in Fig. 3g shows the EDX spectrum.

lattice fringes are measured to be 0.39 nm and 0.22 nm, corresponding to the d-spacing of the (101) and (012) planes, respectively. Similar XRD patterns were obtained for the bare LVO-ROD and C@LVO-ROD (Fig. 3f), suggesting that the introduction of carbon does not change the crystal structure and compositions of LVO. The carbon coating forms a 3D conductive network giving rise to improved electrical conductivity. Moreover, it could suppress the pulverization related to the volume change in LVO nanoparticles upon cycling to some extent, also be beneficial for structural integrity and stability.

Fig. 4 Lithium storage behavior. (a) Rate performance of LVO-ROD and C@LVO-ROD 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⁺, (b) Cycling performance of C@LVO-ROD and LVO-ROD at 0.1 A g⁻¹, (c) Dependence of oxidation peak current on the square root of scan rate for LVO-ROD and C@LVO-ROD, (d) EIS spectra of LVO-ROD and C@LVO-ROD after 100 cycles at a current density of 0.1 A g⁻¹.

The electrochemical performance of carbon-coated sample (C@LVO-ROD) was tested and compared with the bare sample. The C@LVO-ROD delivers specific capacities of 460, 440, 410, 365, 305, and 250 mAh g⁻¹ at rates of 100, 200, 400, 800, 2000, and 4000 mA g⁻¹, respectively (Fig. 4a). Moreover, a discharge capacity of 420 mAh g⁻¹ is still retained upon reducing the current density back to 100 mA g⁻¹, indicating the excellent reversibility. C@LVO-ROD shows higher capacities than those of LVO-ROD at all current rates. The improved cycling performance was also demonstrated by C@LVO-ROD (Fig. 4b). A capacity of 430 mAh g⁻¹ (at 100 mA g⁻¹) is maintained even after 100 cycles, higher than 234 mAh g⁻¹ of bare LVO-ROD. Based on Randles-Sevchik equation, the apparent Li⁺ ions diffusion coefficient of C@LVO-ROD was calculated to be $4.815 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is much higher than that of LVO-ROD ($3.722 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$). The impedances of the two samples after 100 cycles were evaluated using EIS measurements and the typical Nyquist Nyquist plots are fitted by using equivalent circuit model. The simulated parameters are shown in Table 2. As can be seen, the charge transfer resistance (R_{ct}) of C@LVO-ROD is found to be 110 Ω, which is lower than that of the bare LVO-ROD electrode of 180 Ω. Benefiting from these, C@LVO-ROD electrode delivers capacities as high as 250 at 2 A g⁻¹ and 220 mAh g⁻¹ at 4 A g⁻¹ event after 150 cycles. These values are

comparable with those of other reported LVO in literature (summarized in Table S3).

Conclusions

Spherical-assembly LVO-SPHERE, flower shape LVO-FLOWER, single-crystal LVO-ROD nanorods and bulk LVO-BULK were prepared via a solvothermal synthesis method in different alcohols. The effect of LVO morphologies on the electrochemical performance was systematically investigated. The single-crystal LVO-ROD nanorods are found to be advantageous due to the unique 1D structure that is porous and has a small particle size. Therefore, the short lithium ion diffusion length and the large specific surface area facilitate high electron pathway. Further improvement in electrochemical performance was achieved by the surface carbon coating that allows the increase of the electronic conductivity and the suppression of the pulverization caused by volume change in LVO nanoparticles upon cycling. In addition, the findings from the present work promote the better understanding of the morphology controlled Lithium-ion storage in LVO, and provide insight for high-performance LVO-based electrode design.

Conflicts of interest

There are no conflicts to declare.

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