Morphology inheritance synthesis of carbon-coated Li_3VO_4 rods as anode for lithium-ion battery

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ABSTRACT Li_3VO_4 shows great potential as an intercalation/de-intercalation type anode material for energy-storage devices. Morphology tailoring and surface modification are effective to enhance its lithium storage performance. In this work, we fabricate carbon coated Li_3VO_4 (C@LVO) rods by a facile morphology inheritance route. The as-prepared C@LVO rods are 400–800 nm in length and 200–400 nm in diameter, and orthorhombic phase with V^{5+} . The unique core-shell rods structure greatly improves the transport ability of electrons and Li^+ . Such C@LVO submicron-rods as anode materials exhibit excellent rate capability (a reversible capability of 460, 438, 416, 359 and 310 mA h g^{-1} at 0.2, 1, 2, 5 and 10 C, respectively) and a high stable capacity of 440 and 313 mA h g^{-1} up to 300 cycles at 0.2 and 5 C, respectively.

Keywords: carbon coated Li_3VO_4 , morphology inheritance route, high capacitive contribution, lithium-ion batteries

INTRODUCTION

Lithium-ion batteries (LIBs) show vast market value in high-end consumer electronics owing to their high energy density, no memory effect as well as environmental benignity [1–4]. On the basis of the lithium storage mechanism, three kinds of fundamental anode materials were studied: the intercalation/de-intercalation type such as graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiNb_2O_7 [5–7], the alloy/de-alloy type such as Si- and Sn-based alloys [8–10], and the conversion-type such as cobalt metal oxide and other transition metal oxides [11,12]. Among them, the intercalation/de-intercalation type graphite is the most widely employed material as commercial LIBs' anodes. However, the graphite anode faces several challenges such as limited specific capacity (theoretical value $\sim 372 \text{ mA h g}^{-1}$) and safety concerns (dendrite lithium growth during Li^+ intercalation at low potential close to 0 V) [13,14]. So, it is

highly desirable to find anode alternatives with both large capacity and relatively high potential of Li^+ insertion. Another intercalation-type anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is able to improve cell safety with cycling stability due to its high voltage plateau and zero volume change during the cycling [15]. However, its low theoretical capacity ($\sim 175 \text{ mA h g}^{-1}$) and a relatively high voltage plateau at $\sim 1.54 \text{ V}$ vs. Li^+/Li inevitably lead to a low full cell energy density [16].

A new promising intercalation type material, orthorhombic Li_3VO_4 (LVO), was recently reported to be an alternative anode for LIBs. Compared with other anode materials, LVO shows a relatively larger capacity (theoretical value $\sim 394 \text{ mA h g}^{-1}$) than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and a safer working window (0.2–1.5 V vs. Li/Li^+) than graphite [13,17–20]. Moreover, LVO possesses a high ionic conductivity of 10^{-4} – $10^{-6} \text{ S cm}^{-1}$, allowing rapid Li^+ diffusion. However, its low electrode kinetics and electrical conductivity ($< 10^{-10} \text{ S m}^{-1}$) may cause unsatisfactory rate performance and capacity fading [21–23]. To address the low electrode kinetics issue, tailoring morphology of LVO with short diffusion path length of Li^+ is a practical way [17,22,24]. It is well known that one dimensional (1D) nanostructure materials have attracted tremendous attention because of their short diffusion path lengths for ions and facile strain relaxation during battery charge and discharge. For instance, Yang *et al.* [20] and Shen *et al.* [25] demonstrated the excellent electrochemical properties of 1D-structure LVO (nanorods and nanowires) used in LIBs and supercapacitor filed. For addressing the conductivity issue, the hybridization of LVO with conductive carbon materials has been reported to be an effective way to improve the electronic conductivity [22]. On the basis of above, designing LVO that possesses 1D-structure together with carbon coating would realize sy-

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nergetic effect and maximize its electrochemical performance. To obtain carbon coated 1D-structure LVO, the carbonizing process of LVO is required, in which the nanosized LVO rods easily aggregate to be large LVO ones, leading to the disappearance of 1D structure [20]. Thus, it is desired to develop a way to prepare a 1D carbon-coating LVO. Recently, Shen *et al.* [19] synthesized LVO@C sub-micrometer spheres with enhanced performance *via* a morphology-inheritance route, in which the LVO can perfectly maintain spheres after carbon coating. Thus, it can be speculated that 1D carbon-coated LVO (C@LVO) can also be prepared *via* this route, as long as using 1D V_2O_5 as precursor. In the previous studies, polyol-based process was widely applied to control V_2O_5 morphology. For example, we have fabricated Ni- V_2O_5 hollow microspheres by a polyol-based process [26], and additionally Ragupathy *et al.* [27] have prepared V_2O_5 rods *via* the typical polyol method and post calcination treatment. Inspired by these studies, it is highly urgent to design C@LVO rods with outstanding electrochemical performance. However, the related reports are extremely limited.

Herein, we report the preparation of C@LVO rods by a morphology inheritance route. The fabricated C@LVO rods possess a core-shell rod structure with 400–800 nm in length and 200–400 nm in diameter, and result in good transport ability for both electrons and Li^+ . Consequently, the C@LVO rods deliver excellent performance in terms of long-term cycle stability and rate performance. The as-prepared C@LVO rods electrode exhibits stable capacity of 440 and 313 mA h g⁻¹ at current of 0.2 C and 5 C after 300 cycles, respectively, and even at a rate as high as 10 C, a high reversible capacity of 313 mA h g⁻¹ can be retained.

EXPERIMENTAL SECTION

Synthesis of V_2O_5 rods

In a typical synthesis, 200 mg of NH_4VO_3 powder was dispersed in 50 mL ethylene glycol under stirring for 15 min. Then the precursor solution was added to a three-necked flask and refluxed at 180°C for 3 h in the oil bath. After being cooled naturally, the V_2O_5 rods were collected by centrifuging, washing and annealing at 600°C for 2 h in air.

Synthesis of C@LVO rods

The as-synthesized V_2O_5 rods and a stoichiometric amount of LiOH were mixed with different mass of polyethylene glycol (PEG) (10–70 wt.%) in an agate

mortar. Subsequently, solid-state lithiation of V_2O_5 and carbonization of the PEG were simultaneously completed by annealing the above mixture at 650°C in an Ar atmosphere, obtaining the C@LVO. For comparison, the pure LVO without PEG was also prepared in a similar procedure. The final products prepared with different PEG amounts (0, 10, 20, 30, 40, 50, 60 and 70 wt.%) were referred as LVO, C@LVO-10, C@LVO-20, C@LVO-30, C@LVO-40, C@LVO-50, C@LVO-60 and C@LVO-70, respectively.

Material characterizations

The as-prepared samples were identified using X-ray diffraction (XRD, Rigaku SmartLab, Cu K α radiation, $\lambda=1.5406$ Å) operated at 40 mA and 40 kV. A field emission scanning electron microscope (SEM, JEOL-6701F) and a transmission electron microscope (TEM, Hitachi 7700) were applied to observe the sample morphology and structure. High-resolution TEM (HRTEM) observation was carried out on a Hitachi 9500 instrument. Fourier transform infrared (FTIR) spectra were performed on a Bruker Vertex 70v spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB250 X-ray photoelectron spectrometer with Al K α X-ray source. Thermogravimetric analysis (TGA) was conducted on a thermal analyzer (NETZSCH STA 449C) in air at a heating rate of 10°C min⁻¹.

Electrochemical measurements

The electrochemical performances of the samples were tested in coin-typed cells, which were assembled in an Ar-filled glove box with oxygen and water content lower than 0.1 ppm. The working electrode slurry was prepared by dispersing C@LVO rods or LVO sample, super P conductive carbon, and polyvinylidene fluoride (PVDF) binder in *N*-methyl pyrrolidone (NMP) at a weight ratio of 70:20:10. The slurry was uniformly coated on Cu foil current collector and dried in a vacuum oven at 60°C for 12 h. After being roll-pressed, the electrode film was cut into discs (11 mm in diameter). For measurement accuracy, the average mass loading of electrode materials was controlled to be 1 mg cm⁻². Pure Li foil and Celgard 2400 films were applied as the reference electrode and the separator in coin-typed cell, respectively. The electrolyte was 1 mol L⁻¹ LiPF₆ solution in ethylene carbonate and diethyl carbonate (*v/v*=1:1). The cells were pre-aged in air for 20 h for the electrochemical measurements. For full cells, the cathode slurry was prepared by dispersing LiFePO₄, super P conductive carbon, and PVDF binder in

NMP at a weight ratio of 80:20:10. The slurry was uniformly coated on Al foil current collector. The diameter of cathode was 14 mm and the average mass loading of LiFePO_4 was 4.3 mg cm^{-2} . The galvanostatic charge-discharge curves were tested on a battery cycler system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were measured on Zennium electrochemical workstation (ZAHNER, Germany). EIS was recorded in the frequency range from 100 kHz to 0.01 Hz with alternating current (AC) modulus at an amplitude of 5 mV.

RESULTS AND DISCUSSION

The schematic illustration of the synthesis procedure of C@LVO is shown in Fig. 1. The crystallographic structure of the as-prepared V_2O_5 was determined by XRD. As shown in Fig. 2a, the diffraction peaks of the products are consistent with those of the pure orthorhombic V_2O_5 (JCPDS card No. 41-1426) [28]. The sharp diffraction peaks with strong intensity indicate the as-prepared V_2O_5 is well crystallized [29–32]. Fig. 2b presents the XRD

patterns of LVO and C@LVO rods. All the diffraction peaks of LVO and C@LVO rods correspond to the orthorhombic phase LVO (JCPDS card No. 38-1247), indicating that V_2O_5 has completely converted to phase-pure LVO crystals after lithiation. No diffraction peak of carbon is observed in the final C@LVO rods product because the carbon is amorphous.

The fabrication of rod-structured V_2O_5 is the key to the morphology inheritance route for preparing C@LVO rods. In the previous reports [33,34], NH_4VO_3 and EG can generate vanadyl glycolate through a polyol process according to the reaction: $\text{NH}_4\text{VO}_3 + \text{C}_2\text{H}_6\text{O}_2 \rightarrow \text{N}_2 + \text{VO}(\text{CH}_2\text{O})_2 + \text{H}_2\text{O}$ (1).

The vanadyl glycolate was then transformed to V_2O_5 after calcination. In a sealed reaction container, Teflon-lined stainless steel autoclave, N_2 microbubbles formed, and the vanadyl glycolate nanoparticles aggregated around the N_2 microbubbles to minimize their interfacial energy, consequently resulting in the hollow microspheres [27]. However, N_2 microbubbles in the unsealed container (this work) escaped from the condenser, which

Figure 1 Schematic illustration of the formation process of C@LVO rods.

Figure 2 (a, b) XRD patterns of the V_2O_5 , LVO, and C@LVO rods.

lead to the formation of disorderly accumulated V_2O_5 rods [35].

FT-IR spectra of LVO and C@LVO rods are illustrated in Fig. 3a and their assignments are summarized in Table S1. The two sharp peaks at 840 and 470 cm^{-1} in LVO and C@LVO rods, are the characteristic peaks of LVO [36]. The broad absorption band detected at 3,430 cm^{-1} is assigned to the hydroxyl groups on the surface of samples. Another peak at 1,624 cm^{-1} corresponds to the water molecules vibration [37]. The only difference between LVO and C@LVO rods lies in peaks at 1,425 and 1,488 cm^{-1} , which are attributed to amorphous carbon [36,38], suggesting the PEG is completely carbonized after annealing in Ar.

XPS measurement was performed to determine the chemical composition and valence of V in the as-prepared C@LVO rods. The XPS spectrum in Fig. S4a clearly shows the existence of Li, V, O, C. The binding energy located at ~ 517.6 eV can be attributed to V $2p_{3/2}$ electrons, which indicates that the V of C@LVO rods is in the pentavalent state (Fig. 3c) [17,19]. The peak at 55.5 eV can be donated to Li 1s state (Fig. S4b). After deconvolution, the O 1s peak exhibits three sub-peaks at 530.7, 532.3 and 533.4 eV, corresponding to the O_2^{2-} , $-OH$ and H_2O , respectively (Fig. S4c) [39]. From Fig. 3d, three

binding energies at around 284.6, 286.1 and 289.6 eV can be discerned for C 1s peak, respectively. Among them, the lower binding energy at 284.6 eV is assigned to the C=C on the surface of C@LVO rods, and the other two peaks at 286.2 and 289.5 eV corresponding to C-O and C=O bonds, respectively, originate from the carbonated species in the C@LVO rods [40,41]. The structural information of LVO and C@LVO rods was further analyzed by Raman microscopy (Fig. S5). The peaks located at 200–500 and 700–900 cm^{-1} are the characteristic peaks of LVO. As shown in Fig. S5, the intensities of these two peaks for C@LVO rods decrease sharply (only two peaks at 781 and 819 cm^{-1} can be observed in the inset of Fig. S5), which indicates that LVO is well encapsulated by the carbon and thus hardly detectable by Raman spectroscopy [22]. The peaks of C@LVO rods at 1,350 and 1,600 cm^{-1} correspond to the characteristic D-band and G-band of amorphous carbon and the crystalline graphic carbon, respectively. TGA shows that the content of carbon in the C@LVO rods is about 5.9 wt.% (Fig. 3b).

Fig. 4a–f and Fig. S1 reveal the structures and morphologies of different as-prepared samples. Fig. 4a shows that V_2O_5 is stacked with rods with length of about several micrometers. It can also be found that the V_2O_5 rods have a rectangular-shaped cross section and nearly

Figure 3 (a) FT-IR spectra of the LVO and C@LVO rods. (b) TG curve of the C@LVO rods. (c) V 2p XPS spectra of the C@LVO rods. (d) C 1s XPS spectra of the C@LVO rods.

Figure 4 SEM images of (a) V_2O_5 and (d) C@LVO rods. TEM images of (b) V_2O_5 and (e) C@LVO rods. HRTEM images of (c) V_2O_5 and (f) C@LVO rods.

round tips (Fig. 4a, b). The HRTEM image (Fig. 4c) shows obvious lattice fringes with an inter-fringe spacing of 0.43 nm, matching with that of the (001) plane of orthorhombic V_2O_5 [42]. As shown in Fig. 4e, the particle size of C@LVO is less than 1 μm . In addition, the C@LVO retains the short rod-like structure after annealing in Ar (Fig. 4d, e). Compared with the precursor, V_2O_5 rods, the C@LVO rods exhibit reduced particle size. The length of C@LVO rods ranges from 400 to 800 nm, and the diameter is between 200 to 400 nm (Fig. 4e). Such nanosized particles with reduced lithium diffusion length can facilitate sufficient contact between the electrode material and electrolyte and consequently result in favorable diffusion and transport of Li^+ in the electrode. To understand the structure evolution of C@LVO, SEM images of LVO, C@LVO-10, C@LVO-30 and C@LVO-50, C@LVO-70 are also provided in Fig. S1, respectively. From the SEM image of pure LVO in Fig. S1a, we can see that mere lithiation results in the destruction of rod morphology. However, the C@LVO samples can maintain the rod morphology (Fig. S1b–e), indicating PEG is the key to maintaining the rod morphology during the solid-state reaction. When the amount of PEG increases from 10% to 60%, the length of C@LVO rods further shortens. When the amount of PEG further increases up to 70%, the rod morphology is destroyed (Fig. S1f). Fig. 4f shows that a carbon shell with thickness of 5–10 nm is coated onto LVO to form a C@LVO core-shell nanostructure. Such a thin carbon coating on the surface of LVO can serve as an electronic contact to all interconnected LVO particles. In addition, the observed lattice fringes with spacing of 0.41 nm are consistent with that of the (110) plane of LVO [17]. The carbon layer not only

suppresses the LVO growth but also serves as an electronic bridge to connect with the LVO.

To investigate the effect of carbonization process on the LVO crystal growth, LVO and C@LVO samples prepared with different amounts of PEG were characterized by XRD. Fig. S2 shows that all the C@LVO products are the orthorhombic phase, indicating that the adding PEG amount does not affect the LVO phase. Compared with pure LVO without carbon, diffraction peaks of C@LVO get weaker in intensity and wider in breadth with increasing content of carbon, which illustrates that the addition of PEG inhibits the growth of crystalline LVO, consistent with the result of SEM images (Fig. S1). For optimizing the carbon layer, the rate performance of LVO with different carbon contents was also measured and displayed in Fig. S3. It can be found that the rate performance gradually increases firstly and then decreases with increasing amount of PEG. The C@LVO-60 electrode achieves the best rate performance. A bit of PEG facilitates carbon coating on the surface of LVO to enhance its electronic conductivity, while too much PEG hinders the diffusion of Li^+ and results in deteriorative capacity [43]. Thus, the C@LVO-60 is selected as the target C@LVO rods electrode for further electrochemical performance study.

CV was performed to investigate Li^+ storage process of the as-prepared C@LVO rods. Fig. 5a shows the initial three cycle CV curves of C@LVO rods electrode at a scan rate of 0.2 mV s^{-1} . In the first CV curve, one main reduction peak ascribed to the Li^+ insertion can be observed at 0.41 V and two oxidation peaks related to the Li^+ deintercalation process can be discerned at about 1.05 and 1.35 V, in accordance to the galvanostatic discharge-

Figure 5 Electrochemical performance of the C@LVO rods. (a) The first three consecutive CV curves at a scan rate of 0.2 mV s^{-1} . The open circuit potential is ca. 2.2 V. (b) The first five discharge-charge voltage profiles at rate of 0.2 C. (c) Cycle performance and coulombic efficiency at a current rate of 0.2 C. (d) Rate performance at various rates from 0.2 to 10 C. (e) Discharge-charge voltage profiles at different rates from 1 to 10 C. (f) Cycle performance and coulombic efficiency at a current rate of 5 C.

charge voltage profiles (Fig. 5b). In the subsequent two cycles, the reduction peak shifts to 0.73 and 0.5 V, indicating a multi-step Li^+ insertion process within the C@LVO rods after the first cycle. Meanwhile, the observed oxidation peak at 1.05 V in the first cycle disappears. The CV profile at the first cycle is different from those in the subsequent cycles, which may be due to solid electrolyte interface (SEI) formation and phase transformations. Compared with the subsequent second and third cycle curves, highly reproducible CV curves can be observed, revealing the high reversibility of the as-prepared C@LVO rods. The insertion and de-insertion reactions in cycling processes can be described as following equation: $\text{Li}_3\text{VO}_4 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_{3+x}\text{VO}_4$ ($0 \leq x \leq 2$) (2).

The typical galvanostatic charge-discharge curves of C@LVO rods electrode at a current density of 0.2 C (1 C = 400 mA g^{-1}) in the potential window of 0.2–3.0 V (vs. Li^+/Li) are shown in Fig. 5b. A discharge plateau at ~ 0.5 V can be observed from the first discharge curve, corresponding to the cathodic peak at 0.41 V. Meanwhile, the two charge plateaus also match well with the above CV measurement. The C@LVO rods electrode delivers the initial discharge and charge capacity of 516 and $403.4 \text{ mA h g}^{-1}$, which are higher than these of LVO (initial discharge capacity of only 243 mA h g^{-1} at 0.2 C (Fig. S3)). The first coulombic efficiency (CE) is about 78.13%. This relatively large capacity loss mainly origi-

nates from the irreversible side reactions on the anode surface and interface such as the formation of SEI film and other irreversible lithium ions consumption reaction, which is already proved in the CV analysis [44–46]. Interestingly, during the next few cycles, the increase of capacity can be observed in Fig. 5c, d. Such phenomenon might be ascribed to more accessible Li^+ in the electrode materials during the intercalation and de-intercalation process, which strengthens the lithium accommodation [47]. Additionally, from the voltage profiles, it can be easily found that C@LVO rods can deliver 80% of the specific capacity at a relatively safe voltage range from 0.5 to 1.5 V. The long-term cycling performance of C@LVO rods electrode at current density of 0.2 C is presented in Fig. 5c. The C@LVO rods electrode can maintain a discharge capacity of 440 mA h g^{-1} after 300 cycles, and the overall average CE is above 99% except for the first cycle, indicating the superior cycling stability of C@LVO rods.

As shown in Fig. 5d, e and Fig. S3, the rate performance of C@LVO rods was evaluated at different discharge-charge rates. The C@LVO rod electrode shows a larger specific capacity of $\sim 460 \text{ mA h g}^{-1}$ at 0.2 C. As the current density increases from 1 to 2, 5, 10 C, its reversible capacity decreases from 438 to 416, 359, 310 mA h g^{-1} , respectively, and still has a capacity retention as high as $\sim 67\%$ with the current density increased from 0.2 to 10 C (from 80 to $4,000 \text{ mA h g}^{-1}$), confirming its excellent

specific capacity and rate performance. By contrast, the bare LVO electrode almost shows no electrochemical response at 10 C (Fig. S3). Subsequently, when the current density is adjusted from 10 to 0.2 C, the capacity of C@LVO rods electrode goes back to $\sim 450 \text{ mA h g}^{-1}$, which suggests that the highly robust core-shell structure of C@LVO rods is not damaged even at a jumpy current density. Encouragingly, the C@LVO rods electrode still maintains a reversible capacity of 313 mA h g^{-1} after 300 cycles at 5 C (Fig. 5f).

To further elevate the potential of C@LVO rods in practical lithium-ion batteries, the full cell was assembled by using C@LVO rods as anode and commercial LiFePO_4 as cathode. The full cell was tested at a current density of 200 mA g^{-1} in the potential window of 0.5–3.5 V (vs. Li/Li^+). As shown in Fig. S8a, the full cell delivers the initial charge and discharge capacities of 425 and 348 mA h g^{-1} , respectively. Fig. S8b shows that after 50 cycles, the full cell still maintains a charge capacity of 320 mA h g^{-1} . The electrochemical performance of C@LVO rods is also compared with those of other LVO based anode materials reported previously, as summarized in Table S2. The C@LVO rods electrode in this work exhibits excellent cycling performance and high rate performance owing to its inert characteristics shown as follow. First, carbon layer enhances its electronic conductivity and consequently improves the reversibly specific capacity of the

electrode. Second, the C@LVO rods with small particle sizes can not only provide enough Li storage sites but also allow rapid Li^+ transport at both particle/electrolyte interface and bulk particle, finally leading to well rate capabilities [48,49]. Third, this interconnected rod morphology of C@LVO particles can withstand significant stress in the charge and discharge process [29]. Finally, the robust core-shell structure can benefit to volume buffering during lithium insertion/deinsertion, hence retaining structural stability during cycling [50].

The CV curves (Fig. 6a) of the C@LVO electrode at various scan rates are presented to further obtain thorough insights into the charge storage mechanism in the C@LVO rods. Even the sweep rate increasing by 25 times, the position of the current peaks shows no obvious changes. This indicates that C@LVO rod electrode possesses a rapid Li^+ transport kinetics. The exponential relationship between current (i) and scan rate (v) obeys the following equation [51]: $i = av^b$ (3), where a and b are adjustable parameters. The battery-type of lithium ion intercalation kinetics can be distinguished by obtaining the b -value at a given redox potential from plots of the log (scan rate)-log(peak current) curve. Specifically, a typical capacitive (or surface) behavior corresponds to $b=1.0$, whereas a total diffusion-controlled behavior dominates the Li^+ storage reaction at $b=0.5$. Fig. 6b shows the b -values of 0.81 for cathodic and 0.85 for anodic peaks,

Figure 6 (a) CV curves of the C@LVO rods at different scan rates. (b) Determination of the b -value using the relationship between peak current and scan rate (the right redox peaks). (c) The percentage of capacitance contribution at different scan rates. The capacitive contribution to charge storage of the C@LVO rods at different scan rates of (d) 0.2, (e) 3, and (f) 5 mV s^{-1} .

respectively. This suggests that the reaction current at the peak potential is mainly dominated by capacitive process. The contribution of the capacitive process can be quantified at a given potential by deducing from the following equation [52,53]: $i = k_1 v + k_2 v^{1/2}$ (4), where k_1 and k_2 are constant. Note that $i = k_2 v^{1/2}$ and $i = k_1 v$ represent the diffusion limited process and surface-controlled capacitive process, respectively. After dividing both sides of equation (4) by $v^{1/2}$, the above equation can be rewritten as follows [54–56]: $i/v^{1/2} = k_1 v^{1/2} + k_2$ (5).

Then, k_1 and k_2 can be estimated from the slope and the y-axis intercept point by plotting $i/v^{1/2}$ against $v^{1/2}$ (Fig. S6). Based on the k_1 and k_2 , the capacitive contribution at different potentials can be quantitatively calculated and the results are outlined in Fig. 6c–f. As shown in Fig. 6c, when the scan rate increases from 0.2 to 5 mV s^{-1} , the capacitive contribution ratio accordingly increases from 63% to 91%. The high capacitive contribution can explain the high rate performance of the C@LVO rods electrode [57].

EIS shed more light on the electronic transport mechanism of the samples. The typical Nyquist plots with equivalent circuit model (inset) for the C@LVO rods and LVO electrodes after 30 cycles are shown in Fig. 7. The resistance (R_e) of electrodes, separator, and electrolyte can be obtained from the intercept of semicircle in the high-frequency region. R_s reflects the SEI layer's resistance, which can be obtained from the first semicircle in the high-frequency region. The charge transfer resistance (R_{ct}) at the interface between electrode and electrolyte can be obtained from the second semicircle in the medium-frequency range, while the impedance curve (W) is the slope in the low-frequency region, which corresponds to the Li^+ diffusion between the active electrode material and electrolyte [15]. The fitting results obtained from the ZView software are summarized in Table 1. Note that the applied electrolyte and cell device are same, and thus all samples have an almost identical R_e obtained from the fitting result. R_s of C@LVO is smaller than that of bare LVO, originating from the stable core-shell structure of C@LVO anode that could effectively maintains the stability of SEI during the cycling charge-discharge process [58]. The bare LVO electrode has a large R_{ct} of 34.3 Ω , much higher than that of the C@LVO electrode (8.7 Ω). This suggests that the electron movement in bare LVO electrode is more difficult after cycling, which may be due to the pulverization of bare LVO during the cycling process [20]. In the frequency region of 1–10 Hz, the slope of C@LVO electrode impedance curve is steeper than that of LVO, indicating that C@LVO electrode has a

Figure 7 EIS spectra of the LVO and C@LVO rods. All measured after 30 cycles (the AC amplitude was 5 mV, and the frequency range applied was 0.01 Hz to 100 kHz). Inset: the equivalent circuit used to describe the charge process.

Table 1 EIS fitting results for the LVO and C@LVO rods

Samples	R_e (Ω)	R_s (Ω)	R_{ct} (Ω)
LVO	2.94	25.04	34.35
C@LVO rods	3.66	5.57	8.72

faster Li^+ diffusion rate.

CONCLUSIONS

To summarize, we synthesized C@LVO rods by a morphology inheritance route. The C@LVO rods as an anode material shows an excellent cycling stability (440 and 310 mA h g^{-1} after 300 cycles at 0.2 and 5 C, respectively) and high rate capability (310 mA h g^{-1} at 10 C). Such excellent electrochemical performances of C@LVO rods are arising from its core-shell rod structure which can withstand significant stress and facilitate the electron/ion transport during the charge and discharge process. The kinetic analysis reveals that the good cycling stability and high rate capability of the C@LVO rods are associated with the predominant contribution from capacitive behavior. Thus, the C@LVO rod is a highly promising alternative anode material of commercial graphite for LIBs.

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Supplementary information Supporting data are available in the online version of the paper.

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形貌遗传法制备碳包覆棒状 Li_3VO_4 锂离子电池负极材料

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摘要 Li_3VO_4 作为一种能够应用到储能装置上的脱嵌型负极材料展现了巨大的应用潜力。形貌调控和表面修饰是提升 Li_3VO_4 电化学性能非常有效的方法。本文通过一种形貌遗传法制备了碳包覆的棒状 Li_3VO_4 。SEM和TEM结果表明这种碳包覆棒状 Li_3VO_4 材料的长度约为400–800 nm, 直径约为200–400 nm。XRD和XPS结果证明碳包覆棒状 Li_3VO_4 仍然是正交相, 其中V的价态为+5。由于其独特的核壳结构, 它的电子和锂离子的传输能力都有较大的提升。因此, 碳包覆棒状 Li_3VO_4 展现出优异的电化学性能, 在0.2, 1, 2, 5和10 C的电流密度下分别有460, 438, 416, 359和310 $mA\ h^{-1}$ 的可逆容量, 在0.2和5 C的电流密度下循环300圈后仍然具有440和313 $mA\ h^{-1}$ 的可逆容量。