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Superior lithium storage performance of hierarchical porous vanadium pentoxide nanofibers for lithium ion battery cathodes



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ABSTRACT

The hierarchical V_2O_5 nanofibers cathode materials with diameter of 200–400 nm are successfully synthesized via an electrospinning followed by annealing. Powder X-ray diffraction (XRD) pattern confirms the formation of phase-pure product. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) obviously display the hierarchical porous nanofibers constructed by attached tiny vanadium oxide nanoplates. Electrochemical behavior of the as-prepared product is systematically studied using galvanostatic charge/discharge testing, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). It turns out that in comparison to the commercial V_2O_5 and other unique nanostructured materials in the literature, our V_2O_5 nanofibers show much enhanced lithium storage capacity, improved cyclic stability, and higher rate capability. After 100 cycles at a current density of 800 mA g⁻¹, the specific capacity of the V_2O_5 nanofibers retain 133.9 mAh g⁻¹, corresponding to high capacity retention of 96.05%. More importantly, the EIS at various discharge depths clearly reveal the kinetics process of the V_2O_5 cathode reaction with lithium. Based on our results, the possible approach to improve the specific capacity and rate capability of the V_2O_5 cathode material is proposed. It is expected that this study could accelerate the development of V_2O_5 cathode in rechargeable lithium ion batteries.

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1. Introduction

High-energy and power-density energy-storage devices have triggered significant research efforts due to the growing applications such as electric vehicles, hybrid electric vehicles, and other power-supply devices [1–3]. Among the energy-storage devices, rechargeable lithium ion batteries (LIBs) have been one of the most promising candidates for the aforementioned applications owing to some obvious advantages of high energy efficiency, long cycle life, and environment friendliness [4–7]. Unfortunately, even after decades of intensive research, the commercially available cathode materials are capable of exhibiting practical capacity of less than 200 mAh g⁻¹ [8–13], originating from 1e⁻/formula-unit, which seriously limits the further LIBs applications. Therefore, to increase the energy density of LIBs requires the development of electrode

materials with high specific capacities based on multi-electron-reaction system during charge/discharge processes [14–19]. Among the potential cathode materials, layered vanadium pentoxide (V_2O_5), as one of the most-attractive cathode materials, has been extensively studied resulting from its low cost, rich abundance, ease of synthesis, better safety as well as its relatively high theoretical capacity (about 294 mAh g⁻¹ with 2 Li insertions/extractions per unit formula) [20–24]. For this cathode, however, two major problems of poor structural stability and sluggish electrochemical kinetics result in the limited long-term cycling stability as well as low rate capability [25,26].

In comparison to the bulk materials, the 1D nanostructured active materials show the following significant advantages: (1) allowing for efficient 1D electron transport along the longitudinal direction, and decreasing the lithium-ion-diffusion pathway [27]; (2) increasing Li⁺-ion flux at the interface between the active material and the electrolyte owing to the large surface-to-volume ratio [28–30], and thus reducing the charge transfer resistance; (3) improving the structural stability and strain relaxation against

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volume expansion, especially the multi-electron-reaction materials. As a result, the one-dimensional (1D) nanostructure is beneficial of improving the electrochemical activity of electrode materials (e.g. Li storage in MnO₂ nanotubes [31]), increasing the cycle life of electrode materials (e.g. Li storage in VO₂ nanowires [32] and 1D Si/Sn nanowires or nanotubes [33]), and especially enhancing charge/discharge rate capability of electrode materials [32,34]. Based on this strategy, a wide range of 1D V₂O₅ nanostructures have recently been synthesized via various methods such as sol-gel reactions [35], electrodeposition [36], hydrothermal process [37], as well as electrospinning [38], to increase the lithium storage performance of the V₂O₅ cathode material. Among all these methods, the electrospinning is a facile and versatile process, which has been regarded as the preferred method over the other approaches for 1D nanofiber synthesis. For example, Zhang et al. have reported that V_2O_5 nanofibers prepared by an electrospinning exhibited improved performance for LIBs [27]. However, using electrospinning technology to fabricate 1D V₂O₅ nanofibers, all previous studies were involved in the costly toxic organic vanadium source [27,39–41] or the expensive polymeric binder [42], which resulted in some difficulties in the practical application due to the problems of the environment and/or the economy. More importantly, on one side, very few reports focused on the rate capability of 1D V₂O₅ nanofibers electrodes via the electrospinning method. On the other side, the rate capability of V_2O_5 greatly depends on the kinetics behavior. Unfortunately, few research was reported to study the kinetics process of V₂O₅ electrode.

In this study, we successfully developed a modified, facile and effective electrospinning to synthesize V_2O_5 nanofibers by using commercial vanadium pentoxide as precursor material. The asprepared 1D V_2O_5 nanofibers exhibited increased lithium storage performance. More significantly, the EIS of the V_2O_5 nanofibers electrodes at various depths of discharge obviously interpreted the kinetics process during lithium intercalation/deintercalation. To the best of our knowledge, it is for the first time to study the electrospinning derived V_2O_5 nanofibers at a kinetic point of view, which clearly demonstrated why the obtained cathode showed superior electrochemical performance.

2. Experimental details

2.1. Material preparation

The synthesis of 1D V₂O₅ nanofibers is as following. The commercial V₂O₅ (0.3 g) and H₂C₂O₄·2H₂O in a molar ratio of 1:3 were dissolved in 10 mL of deionized H₂O under vigorous stirring at 80 °C for 1 h until a clear dark blue VOC₂O₄ solution (0.33 M) was formed. Then 5 mL of the as-prepared VOC₂O₄ under vigorous stirring at 80 °C for 1 h until a clear dark blue VOC₂O₄ solution a mixture of ethanol (5 mL) and N,N-Dimethylformamide (5 mL), followed by the addition of 1.0 g of poly(vinylpyrrodidone) (PVP, $M_w \approx 1,300,000$) under vigorous stirring at 60 °C, and a clear light blue precursor solution was obtained in 30 min. Subsequently, the well-mixed precursor solution was loaded into a 5 mL glass syringe that was equipped with a 9-gauge stainless steel nozzle. The solution was electrospun at a DC voltage of 15 kV and a flow rate of 1.0 ml h⁻¹. The electrospued nanofibers were collected on aluminum foil. The distance between the nozzle and collector was 15 cm. Finally, the as-collected precursor fibers were annealed in a tube furnace at 500 °C in air for 30 min with a heating rate of 1 °C min⁻¹ to yield the V₂O₅ nanofibers.

2.2. Structural characterization

X-ray powder diffraction (XRD) was performed on a Bruker AXS D8 advance Xray diffractometer at the 2 θ range of 10–70° using Cu K α radiation (λ = 1.5405 Å). Traces software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files was used to identify the material phases. The morphologies of the obtained nanofiber samples were observed by Hitachi-SU8010 type field emission scanning electron microscopy (FE-SEM) under 10 kV accelerating voltage. The microstructure and micro-area chemical composition of the samples were studied by a JEOL JEM-2100F high resolution transmission electron microscopy (HRTEM) operating at 200 kV. The as-synthesized samples were ultrasonically dispersed in ethanol, and then dropped onto carbon-coated copper grids to obtain TEM samples.

2.3. LIB electrode fabrication and performance measurements

The working electrodes were fabricated by using the commercial V₂O₅ or the asprepared $V_2 O_5$ nanofibers as the electrochemical active materials, acetylene black as conducting agent, and polyvinylidene fluoride binder in a weight ratio of 70:20:10, respectively. After being blended in the solvent of N-methyl pyrrolidinone, the mixed slurry was cast uniformly on an aluminum foil, and dried overnight in a vacuum at 80 °C. Subsequently, the electrodes were punched into the disks with the diameter of 10 mm, and the V_2O_5 loading was about 2.0 mg cm⁻². The electrochemical performances of the working electrodes were evaluated in a 2032 coin-type cell, in which the lithium foil was used as the counter electrode and reference electrode, the porous polypropylene as the separator, and 1 M LiPF₆ in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene methyl carbonate (EMC) (1:1:1 by volume) as the electrolyte. The electrochemical cells were assembled in an Ar-filled dry glove box. The electrochemical measurements, including galvanostatic charge-discharge testing, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were performed using a Land CT2001 battery tester and a VersaSTAT 200 electrochemical workstation. The cells were galvanostatically discharged and charged in the range of 2.0-4.0 V (vs Li/Li⁺) at various current densities. The CV curves of the electrochemical cells were recorded in a potential range of 2.0-4.0 V (vs Li/Li⁺) at a scan rate of 0.1 mV s⁻¹. The EIS spectra were systematically measured under different depths of discharge with the frequency ranging from 100 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation.

3. Results and discussion

The surface morphology, micro-area structure and crystallization of the as-synthesized nanofibers were characterized by various techniques. Fig. 1 presents the FE-SEM images of the asprepared electrospun nanofibers with and without annealing. It can be clearly seen that the un-annealed nanofibers had a relatively smooth surface without pores or hierarchical nanostructure (Fig. 1a). As shown in Fig. 1b, the close observation revealed that the nanofibers had an average diameter in a range of 200-400 nm, which is obviously smaller when compared with the previous reports [27,40,41]. The subsequent annealing process still retained the continuous 1D nanostructures. However, a notable change of the surface and length of the nanofibers was observed in Fig. 1c. Interestingly, the short nanoplates with the diameter of about 60 nm and length of 200 nm were formed on the surface of the nanofibers (Fig. 1d), which possibly resulted from the thermal decomposition of VOC₂H₄.

The 1D hierarchical nanofiber structure of the obtained V₂O₅ material with an average diameter around 300 nm can be further confirmed by the TEM image in Fig. 2a. As it was shown, the nanoplates were tightly attached with each other to construct the porous nanofibers, and the magnified TEM image of the V₂O₅ nanoplates in the inset of Fig. 2a clearly confirmed it. The HRTEM image in Fig. 2b clearly indicated that the nanofibers displayed lattice fringes with a spacing of 0.342 nm of V₂O₅, which was consistent with the interplanar distance of (101) planes (JCPDS card no. 89-2483). Moreover, the well-resolved fringes revealed the excellent crystallinity of the V₂O₅ nanorods, which was in good agreement with the corresponding fast Fourier transformation (FFT) patterns shown in the inset of Fig. 2b. It is well worth to note that the [010] direction was perpendicular to the [101] direction, which indicated that the long axial direction of the nanoplates was along the [010] direction, and the *b*-axis preference benefited the increasing of length. The excellent crystalline structure of the V₂O₅ nanoplates is verified by the selected area electron diffraction in Fig. 2c. The energy-dispersive X-ray analysis of the selected nanoplates is shown in Fig. 2d. Besides the Cu signal from TEM sample holder, the existence of oxygen and vanadium indicated the high purity of the obtained porous nanofibers. The weight percentages of V and O elements in the material are 50.48% and 37.78%, respectively, and the calculated atomic ratio of V and O elements was about 1:2.38 that was very close to their molar ratio in V_2O_5 .



Fig. 1. Low- and high-magnification FESEM images of electrospun nanofibers: (a and b) as-spun and (c and d) sintered at 500 °C.



Fig. 2. (a) TEM image of V_2O_5 nanofibers sintered at 500 °C; Inset: the partial magnified TEM image of the attached V_2O_5 nanoplates; (b) high resolution TEM image of the selected area in the inset of Fig. 2a. Inset: the corresponding fast Fourier-transfer transformation pattern; (c) selected area electron diffraction (SAED) image and (d) energy-dispersive X-ray analysis (EDX) of the selected nanoplates, where the existence of copper owing to the copper grids for loading the test material.

The well-crystalline and high-pure V_2O_5 nanofibers are further confirmed by the XRD pattern comparison of the commercial V_2O_5 and V_2O_5 nanofibers shown in Fig. 3a. As seen in Fig. 3a, there was not much evident difference in the peak positions for both samples, and no secondary phase was observed, indicating the obtained nanofibers with the pure V_2O_5 phase. All the diffraction peaks of both samples were indexed to an orthorhombic phase V_2O_5 (JCPDS card no. 89-2483) with the lattice parameters of a = 11.544 Å, b = 4.383 Å, c = 3.571 Å, agreeing well with the literatures [39,41,43]. As it is shown in Fig. 3b, the orthorhombic V_2O_5 had a layered structure consisting of V_2O_5 layers stacking along the *c*-axis [41,44].

Based on the aforementioned results, it can be concluded that the porous V_2O_5 nanofibers were successfully synthesized via an



Fig. 3. (a) XRD patterns of the commercial V_2O_5 and nanofibers V_2O_5 . The vertical lines on the *x*-axis correspond to the standard XRD reflections of orthorhombic V_2O_5 and (b) crystalline structure of layered V_2O_5 .

electrospinning technique, which is illustrated in Scheme 1. As we previously reported [45-47], the high potential at the nozzle tip resulted in the surrounding air ionization, and then a large amount of positive ions (e.g., O^+ , O^{2+}) with high-velocity. These positive ions charged the solution by their bombardment in the surrounding area of the nozzle outlet while they moved towards the aluminum foil. With the help of electrostatic repulsion force, the ejected polymer jet was accelerated toward the collector, and the nanofibers were formed on the aluminum foil after solvent evaporation. In this process, the PVP derived nanofibers played the role of a template to attach amorphous VOC₂H₄, which can be confirmed by the XRD pattern of the VOC₂H₄/PVP composite nanofibers (see Supporting Information, Fig. S1). During the subsequent annealing, both VOC₂H₄ and PVP decomposed, while the nanofibers maintained the 1D morphologies when the phase transition occurred. As a result, the hierarchical V₂O₅ nanofibers with high crystalline state (Fig. 3) were obtained, as indicated by the results of SEM and TEM in Figs. 1 and 2. For a comparison, Fig. S2 (see Supporting Information) shows the low and high magnification FESEM images of commercial V₂O₅. It can be observed that vanadium pentoxide had a micrometer-size with random orientation, and exhibited significant agglomeration. It indicated that

the modified electrospinning method we employed in this study is effective to synthesize 1D V_2O_5 nanofibers.

The cyclic voltammetry (CV) is widely performed to study the oxidation/reduction processes and/or Li intercalation/deintercalation behaviors in the electrode reactions. The cyclic voltammograms (CVs) of the commercial V₂O₅ and the V₂O₅ nanofibers during the second cycle are compared in Fig. 4. For the V₂O₅ nanofibers, three well-fine cathodic peaks positioned at around 3.31, 3.10 and 2.17 V were observed in Fig. 4a, which correspond to a series of phase transformation during lithium ion intercalation into the V_2O_5 crystal, along with the formation of $\varepsilon(Li_{0.5}V_2O_5)$, $\delta(Li_{1.0}V_2O_5)$ and $\gamma(Li_{2,0}V_2O_5)$ phases [48], respectively. The reduction peaks located at around 3.31 and 3.10 V correspond to the intercalation of the first Li in two steps, $V_2O_5 + 0.5Li^+ + 0.5e^- \rightarrow Li_{0.5}V_2O_5$ (1) and $Li_{0.5}V_2O_5 + 0.5Li^+ + 0.5e^- \rightarrow Li_{1.0}V_2O_5$ (2). The second Li is inserted through one single step around 2.17 V. $\text{Li}_{1.0}\text{V}_2\text{O}_5$ + $1.0Li^+ + 1.0e^- \rightarrow Li_{2,0}V_2O_5$ (3). During the subsequent anodic process, the three peaks located at 2.62, 3.34 and 3.51 V are attributed to the extraction of the two Li ions, forming $Li_{1.0}V_2O_5$, $Li_{0.5}V_2O_5$ and V_2O_5 respectively, associated with the V^{4+}/V^{5+} redox couple. The commercial V₂O₅ also showed similar electrochemical response (Fig. 4b). However, unlike the V_2O_5 nanofibers, an additional redox



Scheme 1. Schematic diagram showing the strategy for fabricating hierarchical V₂O₅ nanofibers.



Fig. 4. Cyclic voltammograms of the (a) nanofibers V₂O₅ and (b) commercial V₂O₅ during the second cycle at a scan rate of 0.1 mV s⁻¹. The peak currents were normalized to their active mass. Voltage range: 2–4 V.

couples of the commercial V₂O₅ were observed at about 3.54/3.71 V in the high potential region (Fig. 4b), suggesting the complex structural changes during the redox process, which can be ascribed to the irreversible phase transition of the γ/γ' system [49]. More importantly, in the case of the V₂O₅ nanofibers, the potential difference between the cathodic and anodic peaks for the redox reactions (so-called polarization) were 200, 240, and 450 mV, respectively, which were much lower than those of commercial V_2O_5 (340, 350, and 560 mV). All the redox peak currents of the V₂O₅ nanofibers were much high than those of commercial V₂O₅, which showed the higher electrochemical activity of V_2O_5 nanofibers [31,50], originating from the 1D hierarchical nanostructure of the porous V₂O₅ nanofibers. In addition, the voltages of cathodic peaks of the V₂O₅ nanofibers were centered at around 3.31, 3.10 and 2.17 V, which were about 50 mV higher than those of commercial V_2O_5 , respectively. It indicated greatly improved kinetics of lithium insertion/extraction of the porous V_2O_5 nanofibers [51]. Therefore, the hierarchical V₂O₅ nanofibers are expected to show better electrochemical performance than the commercial V_2O_5 .

The electrochemical performances of the V₂O₅ nanofibers were studied in comparison to the commercial V₂O₅ for rechargeable cathode materials. The typical galvanostatic discharge/charge profiles of the commercial V2O5 and V2O5 nanofibers electrodes at various current densities over a potential window of 2.0-4.0 V are shown in Fig. 5a and b, respectively. At the initial lower current density of 100 mA g⁻¹, the discharge/charge curves of the commercial V₂O₅ showed less obvious three plateaus, suggesting the sluggish electrochemical kinetics. The initial discharge and charge capacities were 214.0 and 218.4 mAh g⁻¹, respectively. As the current density increased to 400 and 800 mA g⁻¹, the discharge capacities significantly decreased down to 123.3 and 61.0 mAh g^{-1} respectively. Furthermore, at high current densities of 1.5 and $3\,A\,g^{-1}\!,$ the capacity of commercial V_2O_5 can even be completely ignored. The low performance is due to the poorer charge transfer kinetics of the commercial V_2O_5 electrode, which can be further supported by Fig. S3 (see Supporting Information) that shows the Nyquist plots for both electrodes at the same discharge state. By contrast, the V₂O₅ nanofibers showed highly improved rate performance (Fig. 5b). Specifically, at the current density of 100 mA g^{-1} , the discharge/charge curves of the V₂O₅ nanofibers showed visible three plateaus, which were consistent with the CV analysis in Fig. 4b. Moreover, the increased initial discharge and charge capacities were 276.3 and 283.5 mAh g^{-1} at 100 mA g^{-1} , respectively, which was close to its theoretical capacity (294 mAh g^{-1}). As the current density increased to 400, 800, and 1500 mA g⁻¹, the

discharge capacities decreased down to 198.5, 139.4, and 91.2 mAh g⁻¹, respectively. Even at a very high current density of 3 A g⁻¹, the V₂O₅ nanofibers electrode can still deliver a capacity of 50.3 mAh g⁻¹. The obtained results obviously demonstrated superior performance of the obtained V₂O₅ nanofibers, and they were better than the nanostructures reported previously, for instance, the nanoparticle [52], nanorods [53], nanowires [42], and hollow microspheres [54]. It is noticeable that the capacity loss with the plateau below 2.5 V was more apparent than that of the plateaus above 2.5 V, which is considered to be an important reason of capacity fade with the increase of the current density.

The rate capability of the commercial V₂O₅ and V₂O₅ nanofibers at various current densities are compared in Fig. 5c. It is obvious that the V₂O₅ nanofibers exhibited much better rate capability and cyclic stability than the commercial V₂O₅. For instance, at a current density of 100 mA g⁻¹, the commercial V₂O₅ electrode experienced a continuous capacity fading in the initial four cycles; by contrast, the specific capacity of V₂O₅ nanofibers reached a relatively stable state after the first three cycles, which can be further verified by Fig. S4 (see Supporting Information) that shows the first four cycles CVs for both electrodes. Interestingly, the specific capacity for V₂O₅ nanofibers was recovered after the cathode electrode worked at various current densities for 45 cycles, which was significantly better than that of the commercial V₂O₅ electrode. Fig. 5d shows a comparison of the capacity retention of both materials. It can be observed that the commercial V₂O₅ electrode experienced rapid capacity fading with increasing the current density when compared with that of V₂O₅ nanofibers electrode. Meanwhile, the relative capacity retention of the commercial V₂O₅ was significantly lower than that of V₂O₅ nanofibers. To further compare cycling performance at high rates, the long-term cyclic stability of both commercial V₂O₅ and V₂O₅ nanofibers at the current density of 800 mA g^{-1} were compared in Fig. 5e and f. It can be observed in Fig. 5e that the specific discharge capacity of commercial V_2O_5 exhibited a continuous capacity fading during the whole test (Fig. 5e). To be specific, the discharge capacity was only 40.6 mAh g⁻¹ after 100 cycles, corresponding to the capacity retention of 71.85%. Conversely, the V_2O_5 nanofibers showed highly improved cycle stability in Fig. 5f. In particular, the discharge capacity of V₂O₅ nanofibers increased after the third cycle, and reached a maximum of 143.6 mAh g^{-1} in the 52th cycle, which is similar to the results reported by Li et al. [50] on the doped V₂O₅ system. Moreover, after 100 cycles, the high discharge capacity of 133.9 mAh g^{-1} was retained with high capacity retention of 96.05%, which is obviously higher than the reported results in Refs.



Fig. 5. Electrochemical properties of the prepared materials: galvanostatic discharge/charge voltage profiles at different rates of the (a) commercial V_2O_5 and (b) V_2O_5 nanofibers; (c) rate and cycling performance of the commercial V_2O_5 and V_2O_5 nanofibers; (d) comparison of the capacity retention. Specific capacity of the (e) commercial V_2O_5 and (f) V_2O_5 nanofibers for 100 cycles at a current density of 800 mA g⁻¹. Inset shows the charge/discharge curves correspond to different cycles.

[27,41–43,52–54]. And, the Coulombic efficiency of V₂O₅ nanofibers can reach as high as 99.92% over 100 cycles, which was slightly higher than that of commercial V_2O_5 (98.97%). It is well worth to note that in comparison to the insets of Fig. 5e and f, the electrochemical polarization of V2O5 nanofibers was much lower than that of the commercial V₂O₅, which agreed well with the results of CVs (Fig. 4). A comparison of the electrochemical performance of our V₂O₅ nanofibers with some representative reported V₂O₅ electrode materials is given in Table 1. All the above evidence provides convincing proof of the excellent rate capability and cyclic stability of as-prepared V₂O₅ cathode material, which can be mainly attributed to the porous 1D hierarchical nanofiber structure that provides efficient 1D electron transport along the longitudinal direction, short distances of Li⁺-ion diffusion, as well as improving electrode-electrolyte contact area for high Li⁺-ion flux across the interface. More importantly, the hierarchical nanoplate structure can effectively alleviate the structural strain and irreversible phase transformation resulted from the repeated lithium intercalation-deintercalation processes [27], which was significantly different from the agglomeration of commercial material that easily led to the irreversible loss of active material, thus significantly ensuring the structural stability and improving the cycle performance of the obtained V_2O_5 nanofibers.

Electrochemical impedance spectroscopy (EIS) is one of the most important electrochemical techniques to understand the kinetics of the Li⁺ ion insertion/deinsertion processes [55-58]. Fig. 6a shows the Nyquist plots of the 1D V₂O₅ nanofibers electrode gathered within the frequency range of 100 kHz to 10 mHz at various depth of discharge (DOD) after the electrode was activated at 40 mA g⁻¹ for 3 cycles. It can be observed that all the spectra displayed two well-defined regions of a depressed semicircle in the high-frequency region and a sloped line in the low-frequency region, which is consistent well with the reported results [59]. The equivalent circuit was employed to simulate the impedance spectra, as shown in the inset of Fig. 6a. In the equivalent circuit, $R_{\rm O}$ represents the electrolyte resistance, which could also be verified by the ionic conductivity of the liquid electrolyte, the electrode area and the distance between the working electrode and the counter electrode; R_{ct} stands for charge transfer resistance between the electrode and the electrolyte; CPE is the double layer capacitance on the electrode surface; and W is the Warburg impedance. Fig. 6b presents the simulated $R_{\Omega} + R_{ct}$ values (diameter of

Table 1

The summarization of electrochemical performances of as-prepared V_2O_5 nanofibers and the V_2O_5 material	previously reported in the literature.
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V ₂ O ₅ materials	Voltage range (V)	Current density (A g ⁻¹)	Initial discharge capacity (mAh g ⁻¹)	Capacity retention (%)	Rate capacity (mAh g ⁻¹) at relevant current density	Ref.
Nanoparticles	2.0-4.0	0.12	250	73.0 (after 60 cycles)	_	[52]
Nanorods	2.0-4.0	0.1	260	56.0 (after 60 cycles)	31 at 2.0 A g^{-1}	[53]
Nanowires	2.0-4.0	0.05	275	68.0 (after 50 cycles)	_	[42]
Hollow microspheres	2.0-4.0	0.08	319	50.1 (after 45 cycles)	120 at 0.4 A g^{-1}	[54]
Nanofibers	1.75-4.0	0.035	316	43.0 (after 50 cycles)	114 at 0.35 Å g^{-1}	[41]
Nanosheets	2.0-4.0	0.3	261	68.9 (after 50 cycles)	140 at 3.0 A g^{-1}	[7]
Hierarchical nanofibers	2.0-4.0	0.8	139	96.0 (after 100 cycles)	91 at 1.5 A g^{-1}	Ours



Fig. 6. (a) Nyquistpolt of V₂O₅ nanofibers electrode measured at various depths of discharge (DOD). (b) The calculated R_Ω + R_{ct} values at the different depth of discharge state.

semicircle at high frequency) under various DOD states. Clearly, the value of $R_{\Omega} + R_{ct}$ continuously increased from 484.2 Ω to 973.6 Ω , and 1086.7 Ω with the DOD increasing from 0% to 63%, and 100%, respectively. It is worth mentioning that the charge transfer resistance with the plateau below 2.5 V (e. g. DOD 63%: 973.6 Ω) was nearly twice higher than that of the plateaus above 2.5 V (e. g. DOD 5%: 540.1 Ω), which is indicative of poorer charge transfer kinetics at the electrode-electrolyte interface when γ -Li_{2.0}V₂O₅ phase is potentially formed (corresponding to the second Li insertion). It indicated that the electrochemical reaction at high DOD shows much more difficult than the one at low DOD. As a result, the specific capacity is hard to deliver when the electrode material is inserted more than 1 Li per unit formula. The important observation could explain why the capacity loss of the plateau below 2.5 V was more with increased current densities in Fig. 4a and b.

Based on the aforementioned results and discussion, some insight information may be drawn to understand the electrochemical performance improvement of V_2O_5 cathode material. Firstly, to design the surface defects and/or increase the porosity of the electrode material by means of physical and/or chemical approaches can greatly enhance electrode–electrolyte contact area to promote the electrochemical reaction, and significantly reduce the charge transfer resistance. Secondly, to reduce the size of the primary particle of the active material will be equally effective to promote the electrochemical activity. Last but not least, doping alien metal ions to tailor the electronic structure and/or crystalline state of the electrode material can also improve the electrochemical kinetics, and thereby enhancing the rate capability.

4. Conclusions

In this study, we have successfully developed a cost-saving approach using low-cost commercial V_2O_5 to synthesize hierarchical porous V_2O_5 nanofibers builded by attached V_2O_5 nanoplates.

As one of the most potential cathode materials for LIBs, the as-prepared V_2O_5 nanofibers exhibited highly rate capacities and superior cycling stability when compared with the commercial V_2O_5 and the previous results reported in the literature. It was confirmed that the obtained excellent electrochemical performance resulted from their unique 1D porous nanostructure. In particular, the kinetics analysis based on the CVs and EIS results revealed that the behavior of Li⁺ ion insertion/deinsertion of the V_2O_5 nanofibers was significantly improved. Moreover, the possible strategies to enhance the rate capability of the V_2O_5 electrode materials were concluded. The facile strategies will enable to help improve the electrochemical performance of the V_2O_5 cathode materials in LIBs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2015.01. 292.

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