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One-step in situ synthesis of ulthathin tungsten oxide@carbon nanowire webs as an anode material for high performance

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Graphical abstract: Ulthathin W₁₈O₄₉@carbon nanowire web anode showed the best cycling performance (889 mAh g⁻¹ after 250 cycles at 200 mA g⁻¹) for the tungsten oxide anode materials used in lithium-ion batteries reported to date.
One-step in situ synthesis of ultrathin tungsten oxide@carbon nanowire webs as an anode material for high performance

Wenhui Zhanga, Lu Yueba, Feng Zhanga, Qinfang Zhanga, Xuchun Guib, Rongfeng Guana, Guihua Houa and Ning Xua

A novel ultrathin W18O49@carbon nanowire web anode material for high performance lithium-ion batteries is synthesized via a facile one-step solvothermal method. Carbon layer is uniformly coated on ultrathin W18O49 nanowire bundles. The electrochemical properties are analyzed by cyclic voltammetry, galvanostatic charge/discharge cycling and electrochemical impedance. W18O49@carbon nanowire web electrode exhibits high lithium storage capacity of 889 mAh g\(^{-1}\) after 250 cycles at 200 mA g\(^{-1}\), which is the best cycling performance for the tungsten oxide anode materials used in lithium-ion batteries reported to date. The improved electrochemical performance can be ascribed to the incorporation of carbon and the unique ultrathin nanowire web architecture of the nanocomposite.

1. Introduction

As an important semiconductor, tungsten oxide (WO\(_3\)) was used in a wide variety of applications such as gas sensors,\(^1\) photocatalysis,\(^2\) electrochromic devices,\(^3\) dye-sensitized solar cells,\(^4\) supercapacitors\(^5\) and lithium-ion batteries.\(^6\)\(^-\)\(^7\) It also has been examined as an anode material for lithium-ion batteries due to its large theoretical capacity (693 mAh g\(^{-1}\)) than graphite (372 mAh g\(^{-1}\)), because the density of tungsten oxide (7.16 g cm\(^{-3}\)) is larger than that of graphite (2.26 g cm\(^{-3}\)), and the volumetric capacity of tungsten oxide is about four times that of graphite.\(^8\)

Recently, many efforts have been made to synthesize kinds of nanostructured tungsten oxide, such as hierarchical WO\(_3\) flowers,\(^6\) mesoporous WO\(_3\),\(^8\) WO\(_3\) nanorods,\(^9\) WO\(_3\) nanowires,\(^10\) chrysanthemum-like WO\(_3\)-0.33H\(_2\)O,\(^11\) and WO\(_3\) hollow nanospheres\(^12\) for application in lithium-ion batteries. However, to date, the obtained specific capacitance/capacity, cycling stability and rate performance of previous tungsten oxide electrode materials have been still too low to meet the requirements of practical applications. It is very urgent to further improve their overall device performance. Nevertheless, as an anode material, tungsten oxide suffers from large structural and volume variation during the charge/discharge processes, and the induced structure change breaks the stability of electrode material, leading to mechanical disintegration and the loss of electrical connection between the active material and current collector, severely decreasing the cycling ability of electrodes. To overcome these problems, a practical and effective strategy is to create tungsten oxide composites by dispersing active nanoparticles in a lithium active/inactive matrix. Carbon has been extensively used as an active matrix due to its relatively low mass, good conductivity, small volume change, and reasonable lithium-insertion capacity. For example, L.N. Gao et al\(^13\) reported WO\(_3\) nanowire arrays/carbon cloth electrode exhibited a high capacity of 662 mAh g\(^{-1}\) after 140 cycles at a 0.28 C rate and excellent rate capabilities. M.P. Yu et al\(^14\) reported WO\(_3\) nanowires/graphene nanocomposite electrode exhibited a reversible lithium storage capacity of 656 mAh g\(^{-1}\) after 100 cycles at 100 mA g\(^{-1}\).

Ultrathin 1D nanostructures including nanotubes and nanowires with ultrathin diameters less than 10 nm have attracted much research attention in the past few years owing to their unique chemical and physical properties.\(^15\)\(^-\)\(^17\) Among various tungsten oxides, non-stoichiometric tungsten oxide of W\(_{18}\)O\(_{49}\) is of great interest owing to the unusual defect structure and promising properties in the nanometer regime.\(^18\)\(^-\)\(^21\) A.M. Cruz et al studied the electrochemical lithium insertion into W\(_{18}\)O\(_{49}\), and thought that the maximum lithium content corresponded to Li\(_{10}\)W\(_{18}\)O\(_{49}\).\(^22\) Up to now, however, the application of W\(_{18}\)O\(_{49}\) in lithium-ion batteries as anode materials has been not reported.

In this work, we reported a novel ultrathin W\(_{18}\)O\(_{49}\)@carbon nanowire web anode material for high performance lithium-ion batteries which was synthesized by using a facile one-step solvothermal method. The first research work investigating ultrathin W\(_{18}\)O\(_{49}\)@carbon nanowire web led to promising electrochemical performance used as an anode material for high performance lithium-ion batteries.

2. Experimental

2.1 Preparation of W\(_{18}\)O\(_{49}\)/C composite

0.4 g WCl\(_4\) and 0.04 g or 0.8 g D-glucose were dissolved in 40 ml of triethylene glycol. The obtained solution was then transferred to a Teflon-lined stainless steel autoclave and heated at 200 °C for 5 h. The precipitate was collected, purified with distilled water, dried at 90 °C and then heat-treated at 450 °C for
2 h in Ar atmosphere. The obtained sample was named as W₁₈O₄₉, W₁₈O₄₉-C₁ and W₁₈O₄₉-C₂, respectively.

The obtained W₁₈O₄₉ sample and 0.4 g D-glucose were dissolved in 40 ml water. The obtained solution was then transferred to a Teflon-lined stainless steel autoclave and heated at 200 °C for 5 h. The precipitate was collected, purified with distilled water, dried at 90 °C and then heat-treated at 450 °C for 2 h in Ar atmosphere. The sample was named as W₁₈O₄₉-C-3.

2.2 Characterization of samples

The morphology of the samples was observed by a scanning electron microscope (SEM; Hitachi S-4800, Japan) with an energy dispersive spectroscopy (EDS) detector and transmission electron microscope (TEM; FEI Tecnai G2 Spirit, USA). The phase identification was performed by X-ray diffraction (XRD; PANalytical Empyrean, Netherlands) from 10° to 70°. The XPS spectra were obtained with ESCALAB250 XPS (Thermo Fisher Scientific, USA). The Brunauer-Emmett-Teller (BET) test was determined by an automated surface area and pore size analyzer (SI-MIP-10/PoreMaster 33, Quanatapheme Instruments, US).

2.3 Characterization of electrochemical performance

The coin cells (CR2025) were assembled to test the electrochemical performance of the as-prepared electrodes. The as-prepared samples were mixed with acetylene black and carboxymethyl cellulose, in a weight ratio of 60:20:20 in an aqueous solution to form homogeneous slurry. The slurry was spread onto a 10 μm thick copper foil and dried at 60 °C for 12 h in a vacuum oven and then pressed to obtain the electrode sheet with a 9-10 μm coating thickness and a loading level of about 1.4 mg cm⁻². The cells were assembled in an Ar filled glove-box, using 1 M LiPF₆ EC/DEC/DME (1:1:1 by volume) as the electrolyte. The cells were charged and discharged galvanostatically in the fixed voltage window from 0.01 V to 3 V on a Shenzhen Neware battery cycler (China) at 25 °C.

EIS was measured by applying an alternating voltage of 5 mV over the frequency ranging from 10⁻² to 10⁵ Hz. In this work, unless otherwise specified, all impedance measurements were carried out after one cycle of the prepared electrode.

3. Results and discussion

The XRD patterns of the obtained samples are shown in Fig. 1a. It can be seen that all the patterns exhibited two intense diffraction peaks which corresponded to the [010] and [020] crystal faces of the monoclinic W₁₈O₄₉ structure (JCPDS card no. 71-2450). All the other diffraction peaks of samples were weak and broad. The XRD patterns strongly indicated that [010] was the possible crystal growth direction of the samples. In order to verify the valence of W element, XPS measurement was performed (Fig. S1), and the W⁴f-level spectrum of W₁₈O₄₉-C₁ was shown in Fig. 1b. This has been deconvoluted into six peaks indicating tungsten in multiple chemical states of W⁶⁺, W⁵⁺ and W⁴⁺ as reported in some earlier studies. The percentages of W⁶⁺, W⁵⁺ and W⁴⁺ state of W₁₈O₄₉-C₁ are 72.5%, 22.5% and 5.0%, respectively. This further confirms that the sample in W₁₈O₄₉ phase.

The morphologies of the samples were studied through SEM and TEM. Fig. 2(a-c) showed that W₁₈O₄₉ possessed urchin-like webs consisting of nanowires with a diameter about 20 nm. Interestingly, TEM images clearly revealed that the nanowires shown in Fig. 2(b-c) were composed of a lot of individual, thinner nanowires. The diameter of the thinner nanowires was only about 0.9 nm. Similar nanowire web morphology was observed for W₁₈O₄₉-C₁ (Fig. 2(d-f)), and a thin carbon layer with the thickness of about 0.6 nm was coated on the nanowire bundles. Fig. 2(g-i) showed that similar nanowire bundles with a thin carbon layer of about 0.6 nm thickness was observed for W₁₈O₄₉-C-2. Fig. 2(j-l) showed that the aggregation of nanowire bundles was observed for W₁₈O₄₉-C-3, and the thickness of carbon layer was about 4 nm.

![Fig. 1](image)

Further results of SEM examination of W₁₈O₄₉-C₁ combined with EDS mapping for the elements O, C and W are shown in Fig. 3. The bright regions corresponded to the presence of the elements O, C and W in Fig. 3b, c and d, respectively, indicating that O, C and W were distributed homogenously throughout the whole area. The C content of W₁₈O₄₉-C₁, W₁₈O₄₉-C₂ and W₁₈O₄₉-C₃ based on EDS analysis is shown in Table 1. The C content of W₁₈O₄₉-C₁, W₁₈O₄₉-C₂ and W₁₈O₄₉-C₃ was about 38.97%, 63.62% and 40.38% (at.%), respectively, indicating that the C content was consistent to the added content of D-glucose.

In order to investigate the electrochemical reaction mechanism, bare W₁₈O₄₉ and W₁₈O₄₉-C₁ anodes were characterized by XRD after charge and discharge. XRD patterns...
Fig. 2 (a) SEM and TEM images of (a-c) W$_{18}$O$_{49}$, (d-f) W$_{18}$O$_{49}$/C-1, (g-i) W$_{18}$O$_{49}$/C-2 and (j-l) W$_{18}$O$_{49}$/C-3.

of the W$_{18}$O$_{49}$ anode during lithium insertion/extraction of the second cycle are shown in Fig. 4. The peaks of Cu and C came from copper foil and conductive graphite, respectively. The peak of 21° came from CMC. After discharge, the diffraction peaks of about 10°, 19°, 23°, 30°, 42° and 47° could be indexed to Li$_x$W$_{18}$O$_{49}$ (0≤x≤40). After charge, the diffraction peaks could be indexed to W$_{18}$O$_{49}$. XRD results demonstrated that the reversible electrochemical reaction between W$_{18}$O$_{49}$ and lithium could be expressed as follows:

\[ \text{W}_{18}\text{O}_{49} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{W}_{18}\text{O}_{49} \quad (0 \leq x \leq 40) \quad (1) \]

CV of W$_{18}$O$_{49}$, W$_{18}$O$_{49}$/C-1 W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 electrodes was recorded between 0.01 V and 3.0 V, as is shown in Fig. 5. For the first cycle of bare W$_{18}$O$_{49}$ electrode, cathodic peaks were observed at about 1.5, 0.6 and 0.3 V, respectively, corresponding to the electro-chemical reduction reaction of W$_{18}$O$_{49}$ with lithium. However, during the following cycles, only one cathodic peak was noticed at about 0.8 V and all the other reduction peaks that appeared in the first cycle almost disappeared. In the anodic polarization of the first cycle, two oxidation peaks with maximum peaks at about 1.1 and 1.6 V were observed, which was associated with the lithium deinsertion processes. Apparently, the electrochemical reaction of W$_{18}$O$_{49}$ with lithium involved multi-steps for its decomposition and formation. The cathodic peak at 0.8 V and anodic peak at 1.1 V consisted of the main electrode reaction in lithium insertion and deinsertion processes as an oxidation-reduction couple. For the W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 electrodes, there were basically consisted with W$_{18}$O$_{49}$ in CV curves. Nevertheless, besides the clear reduction peak in every cycle, both W$_{18}$O$_{49}$/C-1 and W$_{18}$O$_{49}$/C-3 electrodes displayed a higher peak current, indicating a better electrode reaction happened of that than W$_{18}$O$_{49}$ and W$_{18}$O$_{49}$/C-2.
The charge-discharge voltage profiles of W$_{18}$O$_{49}$, W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 at a current density of 100 mA g$^{-1}$ between 0.01 V and 3.0 V (vs. Li/Li$^+$) were displayed in Fig. 6. The open circuit voltage of these cells laid at about 3.1 V. During the first insertion process, an obvious discharge curve profile was observed for W$_{18}$O$_{49}$ electrode, due to the insertion of lithium ions into the W$_{18}$O$_{49}$ host. Electrochemical reactions of W$_{18}$O$_{49}$ with lithium involved multi-step for its decomposition and formation. There were three discharge voltage plateaus (1.5, 0.6 and 0.3 V) and two charge voltage plateaus (1.1 and 1.6 V) observed in the initial discharge and charge process, which agreed well with its CV curve profile. The highest discharge capacity of 1239 mAh g$^{-1}$ was obtained in the first cycle, which is significantly higher than the tungsten oxide materials reported to date. However, the W$_{18}$O$_{49}$ electrode showed a low initial charge capacity of 543 mAh g$^{-1}$ with a low initial coulomb efficiency of only 43.8%. The irreversible capacity could be assigned to the decomposition of electrolyte, forming a solid/electrolyte interphase on the electrode surface, and leading to the irreversible insertion of lithium ions into W$_{18}$O$_{49}$ host [27]. In the subsequent cycles, the discharging curves were different from the first discharge, while charging curves were identical with the first curve. The subsequent discharging curves became very smooth. As comparison, there were two non-obvious discharge voltage plateaus (0.7 and 0.3 V) observed in the initial discharge process for W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 electrodes. They showed an improved initial coulomb efficiency of 66.8%, 70.8% and 59.5% due to the carbon layer protection, respectively. Specifically, the W$_{18}$O$_{49}$/C-1 electrode showed the best cycling performance, exhibiting the highest charge/discharge capacity of 731/745 mAh g$^{-1}$ and 811/828 mAh g$^{-1}$ at the 50th and 80th cycle, respectively.

The cycling performances of W$_{18}$O$_{49}$, W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 at a current density of 100 mA g$^{-1}$ were compared in Fig. 6. The specific capacity decreased slightly with increasing cycle numbers and the cyclic stability of the W$_{18}$O$_{49}$/C-1 electrode was much better than the other samples. The cycle capacities of W$_{18}$O$_{49}$/C-1 were 1239, 1120, 1050, 930, 860 and 800 mAh g$^{-1}$ at 1, 2, 3, 4, 5 and 6 cycles, respectively, which were much higher than those of W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3. These results indicated that the W$_{18}$O$_{49}$/C-1 electrode exhibited the highest discharge capacity among the three samples.

The discharge-charge voltage profiles of W$_{18}$O$_{49}$ and W$_{18}$O$_{49}$/C-1 anodes are shown in Fig. 6. The specific capacity values were calculated using the following equation:

$$\text{Specific capacity} = \frac{\text{Charge capacity}}{\text{Mass of active material}}$$

where the charge capacity was obtained from the charge profiles and the mass of active material was determined by the weight of the anode. The specific capacity of W$_{18}$O$_{49}$/C-1 was calculated to be 1239 mAh g$^{-1}$ at the 1st cycle, which was much higher than that of W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3. However, the specific capacity of W$_{18}$O$_{49}$/C-1 decreased to 800 mAh g$^{-1}$ at the 6th cycle, which was still higher than that of the other two samples.

The cycling performances of W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 were compared in Fig. 6. The specific capacity of W$_{18}$O$_{49}$/C-1 was calculated to be 1239 mAh g$^{-1}$ at the 1st cycle, which was much higher than that of W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3. However, the specific capacity of W$_{18}$O$_{49}$/C-1 decreased to 800 mAh g$^{-1}$ at the 6th cycle, which was still higher than that of the other two samples.
and 200 mA g⁻¹ were displayed in Fig. 7(a/b). At 100 mA g⁻¹, the W₁₈O₄₉/C-1 electrode delivered a high initial charge/discharge capacity of 808/1210 mAh g⁻¹ and exhibited a high average discharge capacity of 700 mAh g⁻¹ for the first 40 cycles. Then, the capacity increased gradually and the discharge capacity of 872 mAh g⁻¹ over 100 cycles was obtained, which was possibly attributed to some long-term activation process in the W₁₈O₄₉ electrode during charge/discharge reactions. Compared with W₁₈O₄₉/C-1, W₁₈O₄₉/C-2 electrode delivered a lower initial charge/discharge capacity of 652/921 mAh g⁻¹, but a better coulombic efficiency of 70.8%. It was known that the carbon layer on the surface of oxide materials might sacrifice some lithium storage capacity, but also act as a protective layer to prevent the volume expansion and improve the electronic conductivity. As a result, W₁₈O₄₉/C-2 electrode displayed an improved coulombic efficiency but delivered a lower capacity when compared with W₁₈O₄₉/C-1. The W₁₈O₄₉/C-3 electrode also delivered a high initial charge/discharge capacity of 770/1298 mAh g⁻¹ with a coulombic efficiency of 59.3%. However, it exhibited a lower discharge capacity of 647 mAh g⁻¹ over 100 cycles compared with W₁₈O₄₉/C-1. The capacity retention ratio of W₁₈O₄₉/C-1, W₁₈O₄₉/C-2 and W₁₈O₄₉/C-3 electrode was 45.2, 72.1, 44.4 and 49.8% over 100 cycles, respectively. At 200 mA g⁻¹, the electrodes showed similar results. The W₁₈O₄₉/C-1 electrode displayed a better cycling performance, which delivered an initial charge/discharge capacity of 682/946 mAh g⁻¹ with a coulombic efficiency of 72.1% and exhibited an increasing trend of the capacity after 45 cycles and the discharge capacity of 751 mAh g⁻¹ over 100 cycles. The less content of C in the W₁₈O₄₉/C composite was also studied, as shown in Fig. S2. The results show that W₁₈O₄₉/C-1 exhibited the best cycling performance due to suitable carbon content. The rate capabilities of the electrodes are shown in Fig. 7c. The electrodes were cycled at a current density of 100 mA g⁻¹ for the initial 6 cycles. Then the current density was increased gradually to 2000 mA g⁻¹ and finally returned to 100 mA g⁻¹. The W₁₈O₄₉/C-1 electrode showed a first charge/discharge capacity of 649/1212 mAh g⁻¹ with a coulombic efficiency of 53.5%. After 6 cycles, the coulombic efficiency was increased to 98%. At a higher current density of 200, 500, 1000 and 2000 mA g⁻¹, the capacity dropped to about 392, 267, 163 and 92 mA g⁻¹ for W₁₈O₄₉ electrode, 472, 318, 208 and 131 mA g⁻¹ for W₁₈O₄₉/C-2 electrode and 560, 361, 229 and 136 mA g⁻¹ for W₁₈O₄₉/C-3 electrode, respectively. The long-term cycling performance and the coulombic efficiency of the W₁₈O₄₉/C-1 electrode at a current density of 200 mA g⁻¹ are shown in Fig. 7d. The W₁₈O₄₉/C-1 electrode exhibited an increasing trend of the capacity after 45 cycles and the discharge capacity of 889 mAh g⁻¹ over 250 cycles, and then stabilized to 801 mAh g⁻¹ over 300 cycles. As far as we know, this is the best cycling performance for the tungsten oxide anode materials used in lithium-ion batteries reported to date.

To investigate the influence of electrochemical performance, EIS was employed to characterize the impedance properties of W₁₈O₄₉/C-1, W₁₈O₄₉/C-2 and W₁₈O₄₉/C-3 electrodes. The Nyquist complex plane impedance plots of the electrodes after the first two charge–discharge cyclic processes were presented in Fig. 8. It can be seen that all the Nyquist plots included two semicircle parts and one 45° linear diffusion drift for these
electrodes. The $1^\text{st}$ depressed semicircle at the high-frequency were contributed to the resistance of the interphase electronic contacts between the current collector and the solid electrolyte interface (SEI) film; the $2^\text{nd}$ semicircle at the middle-frequency was due to the impedance of the charge transfer reaction at the interface of electrolyte and active material; the inclined line at the low frequency corresponded to the lithium ion diffusion process within the carbon electrodes 31, 32. Based on the behavior of these EIS spectra and the aforementioned studies, a suggested equivalent circuit for the Nyquist plots of these electrodes was shown in Fig. 9(a) inset. This equivalent circuit was consisted of a series of four resistors elements, three constant phase elements (CPE) and a Warburg diffusion element. In the equivalent circuit, $R_1$ was composed of the electrolyte resistance ($R_e$) and the electrode resistance ($R_a$); $R_2$ represented the SEI film resistances; $R_3$ represented the interphase electronic contacts resistance; $R_4$ was the charge-transfer resistance across electrode/electrolyte interface; CPE$_1$ and CPE$_2$ was attributed by the lithium-ion diffusion in the SEI film and pore channel of the electrode materials, respectively; CPE$_3$ represented the electric double-layer capacitance of electrode/solution interface; the $Z_W$ represented Warburg impedance was related to the semi-infinite diffusion of lithium ions into the bulk electrode 33.

![Fig. 8 Nyquist plots for W$_{18}$O$_{49}$, W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 electrodes; the spots correspond to the experimental data; the solid lines stand for the calculated data. Equivalent circuit used to model the impedance spectra.](image)

The fitted impedances (solid lines in Fig. 8) using the equivalent circuit agreed well with the actual impedance data. The corresponding parameters were obtained and summarized in Table 2. The resistance change of $R_1$ was similar for both W$_{18}$O$_{49}$ and W$_{18}$O$_{49}$/C composites. Compared to the W$_{18}$O$_{49}$ electrode, the decrease of $R_2$ in W$_{18}$O$_{49}$/C composites was observed. That is because a stable SEI film was formed after carbon coating, which decreased the resistance for lithium ion migration through the surface film 34. The smaller $R_1$ was also observed in W$_{18}$O$_{49}$/C composites, which usually favored the fast transport of lithium ions and the electrons across the interface. It also indicated that the carbon layer supplied fast charge-transfer channels on the interface of W$_{18}$O$_{49}$ and electrolyte. The $Y_{0.1}$, $Y_{0.2}$ and $Y_{0.3}$ of the W$_{18}$O$_{49}$/C composite electrodes were higher than that of W$_{18}$O$_{49}$ electrode. The increase of $Y_{0.3}$ representing the electric double-layer capacitance favored the charge transfer for the electrode reaction. And the increase of $Y_{0.1}$ and $Y_{0.2}$ favored the diffusion of lithium ion in the SEI film and within the pore channels in the electrode, respectively 35, 36. W$_{18}$O$_{49}$/C-1 electrode owned the least value of $R_a$, corresponding to the charge-transfer resistance in the electrode/electrolyte interface, which was about one-third and one-second of that for the W$_{18}$O$_{49}$ electrode and W$_{18}$O$_{49}$/C-3. Moreover, the value of $Y_{0.3}$ for W$_{18}$O$_{49}$/C-1 electrode was also the highest compared to other electrodes. Based on the above EIS analysis, W$_{18}$O$_{49}$/C-1 electrode exhibited favorable kinetic behavior, the lowest resistance and the highest capacitance, thus best cycling and rate performance among the tested samples. The impedance spectra of the W$_{18}$O$_{49}$/C-1 electrode in the delithiated state after different cycles are also shown in Fig. 9. With the increase of cycling, the semidiameter of the arc part decreased gradually in the Nyquist plots. It indicated that the cycles increased the activation grade in battery, which could improve the charge-transfer channels and reduce the residence on the interface of W$_{18}$O$_{49}$ and electrolyte. This phenomenon was consistent with the increase of capacity with cycling.

![Fig. 9 Nyquist plots for W$_{18}$O$_{49}$/C-1 electrode after 1, 5, 10, 50 and 100 cycles.](image)

Electrochemical properties of tungsten oxide and its composite with carbon by different processes are shown in Table 3. In can seen that ulthatin W$_{18}$O$_{49}$@carbon nanowire web anode material is the highest capacity value for the tungsten oxide and its composite with carbon used in lithium-ion batteries reported to date. The good cyclability of W$_{18}$O$_{49}$/C-1 could be ascribed to their homogenous carbon coated 1D and web-like nanostructures. Because carbon material coated on oxide particle surface could serve as a buffer layer to protect the inner active materials from huge volume changes, and significantly increase the electronic conductivity; the prepared nanostructured webs could improve the interconnectivity and increase the active sites on their surfaces; 1D nanostructures could accommodate the strain during lithium insertion/extraction and the pulverization of materials could be avoided.

The specific surface areas of W$_{18}$O$_{49}$, W$_{18}$O$_{49}$/C-1, W$_{18}$O$_{49}$/C-2 and W$_{18}$O$_{49}$/C-3 were examined by the BET method and were 61.8, 81.3, 60.1 and 59.4 m$^2$/g, respectively. Owing to the fact that a higher specific surface area increased the contact of the electrode and electrolyte, the W$_{18}$O$_{49}$/C-1 electrode was anticipated to show a better electrochemical property.
We reported a novel ultrathin W_{18}O_{49}@carbon nanowire web anode material for high performance lithium-ion batteries which was synthesized via a facile one-step solvothermal method. Carbon layer was uniformly coated on ultrathin W_{18}O_{49} nanowires bundles. W_{18}O_{49}@carbon nanowire web electrode exhibited high reversible capacity of 889 mAh g^{-1} over 250 cycles at 200 mA g^{-1}, excellent cycling performance, remarkable rate capability and enhanced long-term cycling performance compared with the bare W_{18}O_{49} nanowire electrode and W_{18}O_{49}@carbon nanowire web electrode prepared with two-step solvothermal/hydrothermal method. As far as we know, this is the best cycling performance for the tungsten oxide anode materials used in lithium-ion batteries reported to date.

### Table 2 Fitting parameters for the Nyquist plots in Fig. 8.

<table>
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<tr>
<th>Sample I.D.</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$R_3$ (Ω)</th>
<th>$R_4$ (Ω)</th>
<th>$Y_{0,1}$ (μF)</th>
<th>$n$</th>
<th>$Y_{0,2}$ (μF)</th>
<th>$n$</th>
<th>$Y_{0,3}$ (μF)</th>
<th>$n$</th>
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<tbody>
<tr>
<td>W_{18}O_{49}</td>
<td>3.88</td>
<td>18.15</td>
<td>117.20</td>
<td>112.70</td>
<td>2.50</td>
<td>1.07</td>
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</tr>
<tr>
<td>W_{18}O_{49}/C-3</td>
<td>5.28</td>
<td>7.98</td>
<td>100.30</td>
<td>79.75</td>
<td>4.22</td>
<td>1.02</td>
<td>5.92</td>
<td>0.80</td>
<td>175.60</td>
<td>0.64</td>
</tr>
</tbody>
</table>

$Y_0$ and $n$ are two parameters of the constant-phase element

### Table 3 Electrochemical properties of tungsten oxide and its composite with carbon by different processes.

<table>
<thead>
<tr>
<th>The structure of material</th>
<th>Coulombic efficiency (%)</th>
<th>Specific discharge capacity (mAh g^{-1})</th>
<th>Rate capability (mAh g^{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>hierarchical WO_3 Flowers</td>
<td>~70.4</td>
<td>470 after 25 cycles at 50 mA g^{-1}</td>
<td>~450 (100 mA g^{-1})</td>
<td>[6]</td>
</tr>
<tr>
<td>WO_3 thin films</td>
<td>85.8</td>
<td>626 after 60 cycles at 0.02 mA cm^{-2}</td>
<td>/</td>
<td>[7]</td>
</tr>
<tr>
<td>mesoporous WO_3</td>
<td>/</td>
<td>~400 after 30 cycles at 0.2 C</td>
<td>/</td>
<td>[8]</td>
</tr>
<tr>
<td>WO_3 nanorods</td>
<td>~72</td>
<td>607.2 after 30 cycles at 0.05 C</td>
<td>/</td>
<td>[9]</td>
</tr>
<tr>
<td>chrysanthemum-like WO_3-0.33H_2O</td>
<td>~85.2</td>
<td>370.7 after 20 cycles at 50 mA g^{-1}</td>
<td>~290 (100 mA g^{-1})</td>
<td>[11]</td>
</tr>
<tr>
<td>WO_3 hollow nanospheres</td>
<td>74.0</td>
<td>294 after 100 cycles at 0.2 C</td>
<td>~645 (200 mA g^{-1})</td>
<td>[12]</td>
</tr>
<tr>
<td>WO_3 nanowire arrays/carbon cloth</td>
<td>55</td>
<td>622 after 140 cycles at 0.28 C</td>
<td>336 (1C)</td>
<td>[13]</td>
</tr>
<tr>
<td>WO_3 nanowires/graphene</td>
<td>67.4</td>
<td>622 after 100 cycles at 100 mA g^{-1}</td>
<td>500 (200 mA g^{-1})</td>
<td>[14]</td>
</tr>
<tr>
<td>WO_3 nanowires</td>
<td>50</td>
<td>234 after 100 cycles at 100 mA g^{-1}</td>
<td>270 (200 mA g^{-1})</td>
<td>[14]</td>
</tr>
<tr>
<td>W_{18}O_{49}@carbon nanowire web</td>
<td>60.6</td>
<td>889 after 250 cycles at 200 mA g^{-1}</td>
<td>434 (500 mA g^{-1})</td>
<td>our work</td>
</tr>
<tr>
<td>W_{18}O_{49}</td>
<td>43.8</td>
<td>508 after 100 cycles at 200 mA g^{-1}</td>
<td>267 (500 mA g^{-1})</td>
<td>our work</td>
</tr>
</tbody>
</table>

4. Conclusions

We reported a novel ultrathin W_{18}O_{49}@carbon nanowire web anode material for high performance lithium-ion batteries which was synthesized via a facile one-step solvothermal method. Carbon layer was uniformly coated on ultrathin W_{18}O_{49} nanowires bundles. W_{18}O_{49}@carbon nanowire web electrode exhibited high reversible capacity of 889 mAh g^{-1} over 250 cycles at 200 mA g^{-1}, excellent cycling performance, remarkable rate capability and enhanced long-term cycling performance compared with the bare W_{18}O_{49} nanowire electrode and W_{18}O_{49}@carbon nanowire web electrode prepared with two-step solvothermal/hydrothermal method. As far as we know, this is the best cycling performance for the tungsten oxide anode materials used in lithium-ion batteries reported to date.
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Notes and References