

# Achieving Ultrahigh-Rate and High-Safety Li<sup>+</sup> Storage Based on Interconnected Tunnel Structure in Micro-Size Niobium Tungsten Oxides

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Developing advanced high-rate electrode materials has been a crucial aspect for next-generation lithium ion batteries (LIBs). A conventional nanoarchitecturing strategy is suggested to improve the rate performance of materials but inevitably brings about compromise in volumetric energy density, cost, safety, and so on. Here, micro-size Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub> is synthesized as a durable high-rate anode material based on a facile and scalable solution combustion method. Aberration-corrected scanning transmission electron microscopy reveals the existence of open and interconnected tunnels in the highly crystalline Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub>, which ensures facile Li<sup>+</sup> diffusion even within micro-size particles. In situ high-energy synchrotron XRD and XANES combined with Raman spectroscopy and computational simulations clearly reveal a single-phase solidsolution reaction with reversible cationic redox process occurring in the NWO framework due to the low-barrier Li<sup>+</sup> intercalation. Therefore, the micro-size Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub> exhibits durable and ultrahigh rate capability, i.e., ≈130 mAh g<sup>-1</sup> at 10 C, after 4000 cycles. Most importantly, the micro-size  $Nb_{14}W_3O_{44}$  anode proves its highest practical applicability by the fabrication of a full cell incorporating with a high-safety LiFePO<sub>4</sub> cathode. Such a battery shows a long calendar life of over 1000 cycles and an enhanced thermal stability, which is superior than the current commercial anodes such as Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.

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Rechargeable lithium ion batteries (LIBs) have become the dominant electrochemical energy storage technology due to the advantage of high energy density over its rivals (>150 Wh kg<sup>-1</sup>).<sup>[1]</sup> With the urgent pressure of global warming and fossil-fuel depletion, tremendous efforts have been devoted to expand LIBs from widely used potable electronics to large-scale applications such as electric vehicles (EVs) and smart grids, triggering progress in developing high-energy electrode materials in the last few decades.<sup>[2]</sup> As first applied in the early 1990's, the commercial graphite anode has been well developed and almost approached its theoretical capacity limit (372 mAh  $g^{-1}$ ). However, the charging rate of graphite, hindered by the sluggish Li<sup>+</sup> diffusion kinetics, still fails to meet the consumer's demands and actually has become the major concern in the EV industry.<sup>[3]</sup> In addition, safety characteristic is another technical obstacle for the graphite-based LIBs to be used at high rates: the extremely low operating voltage of graphite (≈0.1 V vs Li<sup>+</sup>/Li) leads to Li

dendrite formation, which brings about risks of internal short circuit and battery thermal runaway.<sup>[4]</sup> Therefore, developing high-energy anode materials with higher rate, safer operation, as well as the potential to be facilely scaled up, is becoming an urgent and challenging task nowadays.

The classical LIB-based electrode reactions involve the solidstate diffusion of Li ions in an open host structure, accompanied with electrons transferring along the band structure. In this context, the high rate capability of electrode materials relies critically on the facile kinetics of lithium and electron transports. To date, strategies to achieve high-rate electrodes have mostly focused on the adoption of nano-sized or nanoarchitectured (i.e., coated, porous, hierarchical, and so on) materials due to the reduced lithium and electron diffusion paths.<sup>[5]</sup> However, this design inevitably lowers the packing density of electrodes, and the increased interface between electrode and electrolyte also results in deleterious side reactions. Furthermore, these elaborated nanoarchitectures, in many cases, are fragile and easy to collapse, so the electric and mechanical contacts for fast kinetics are unsustainable with the repetitive strains imposed by long-term electrode reactions.<sup>[6]</sup> In addition to the above, there are also challenges including high cost, low product yield, overlong time consumption, and complex synthetic control, which further limits the industrial applicability of nanosized electrode materials.

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As an alternative approach to nanosizing, developing micro-scale electrode materials for high-rate LIBs has drawn more and more attentions in recent years. The key concept of this effort is to explore materials with open host lattice for facile solid-solution diffusion, continuous band structure for favorable electrical conductivity, and appropriate operating potential (>1.0 V vs Li<sup>+</sup>/Li) for the safety of high-rate LIBs. Based on the above criteria, titanium- and niobium-based oxides, which possess safe potential ranges of 1-2 V (vs Li<sup>+</sup>/Li), have been recognized as promising high-rate anode materials used at micrometer level.<sup>[7]</sup> Among them, spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is the most intensively studied candidate for high-rate LIBs due to the relatively high lithiation potential of  $\approx 1.55$  V that eliminate the risks of forming Li dendrites essentially.<sup>[8]</sup> Unfortunately, the rate capability of this well-established anode material drops severely (e.g.,  $\approx 65 \text{ mAh g}^{-1}$  at 10 C) as the particle size reaches to 1 µm, and other key drawbacks, including poor electrical conductivity and low theoretical capacity (175 mAh g<sup>-1</sup>), also impeded its large-scale energy-storage applications.<sup>[9]</sup> On the other hand, niobium-based oxides with crystallographic shear (or Wadsley-Roth) phases, such as  $Nb_2O_5$ ,  $ANb_{11}O_{29}$  (A = Fe, Cr, and Ga),  $Ti_2Nb_{2x}O_{5x+4}$  (x = 2, 5, and 24),  $Nb_{16}W_5O_{55}$ , and Nb<sub>18</sub>W<sub>16</sub>O<sub>93</sub>, form a fascinating family of high-rate anode materials and recently have been developed to be loaded at micrometer scale.<sup>[10]</sup> The rich and reversible Nb<sup>3+</sup>/Nb<sup>4+</sup> and Nb<sup>4+</sup>/Nb<sup>5+</sup> redox couples enable their high theoretical capacities (over 250 mAh g<sup>-1</sup>). More importantly, from the structural viewpoint, these materials are formed by corner-sharing octahedral blocks connected with edge-sharing octahedral joints. This type of open framework structures offers three-dimensional interconnected highways for both ionic and electronic transports, which thereby makes high-rate energy storage in micrometer-scale particles possible. Despite the efforts, nevertheless, studies on developing novel anode materials with high performance at micro-scale level are highly desirable but still limited to tackle the barriers.

Here, we report the synthetic design, electrochemical properties, and intrinsic mechanisms of micro-size niobium tungsten oxide, Nb14W3O44 (NWO), as a novel anode material for ultrahigh-rate and high-safety LIBs. The unique structural merits of open, stable and interconnected tunnels, demonstrated by scanning transmission electron microscopy (STEM), ensure the favorable electrochemical performance of micro-sized NWO particles. Comprehensive methods, including in situ synchrotron high-energy X-ray diffraction (XRD), in situ X-ray absorption near-edge spectroscopy (XANES), ex situ Raman spectroscopy, galvanostatic intermittent titration technology (GITT) measurements, and theoretical calculations reveal that the NWO framework undergoes a fast solid-solution intercalation process with negligible phase transformation and low energy barrier for Li<sup>+</sup> migration, leading to high Li<sup>+</sup> diffusion coefficient and excellent structural stability during cycling. As a result, the micro-size NWO exhibits excellent rate performance (a high and reversible capacity of  $\approx$ 130 mAh g<sup>-1</sup> at 10 C after 4000 cycles) and superior safety performance. In addition, a  $Nb_{14}W_3O_{44}/LiFePO_4$  full cell also shows long-term cycle life (91.1% capacity retention after 1000 cycles at 10 C).

Micrometer-size NWO particles were successfully prepared through a facile solution combustion method as illustrated in Figure 1a. First, the starting components (the oxidizers and fuel) are dissolved in aqueous solution, in which niobium oxalate and ammonium metatungstate are the source of Nb5+ and W<sup>6+</sup>, and a certain amount of nitric acid was also added to prevent the hydrolysis of Nb5+ to form Nb(OH)5 precipitate. It is worth noting that glycine not only plays the role of fuel, but also forms complexes with metal ions, facilitating the solubility and avoiding partial precipitation of metal ions during rapid water evaporation. After placing in a muffle furnace preheated to 700 °C, the solution was rapidly boiled, ignited, and burned as a flame due to the self-sustained redox exothermic reactions, and the entire combustion duration only took about 1 min. Benefiting from the perfect mixed state of the initial solution at the molecular level and a large amount of gaseous by-products  $(N_2, CO_2, and H_2O)$  generated during the solution combustion process, homogenous and finely dispersed NWO particles can be yielded. The SEM image reveals a brick-like morphology for all the NWO particles, possessing a uniform dimension of about 5–10  $\mu$ m in length and  $\approx$ 2  $\mu$ m in width (Figure 1b). The microstructure of NWO is also confirmed by high-resolution TEM (HR-TEM). Obvious lattice fringes with the interplanar distance of 0.354 nm can be observed, which is consistent with the (211) crystalline plane of NWO (Figure 1c). The selected area electron diffraction (SAED, Figure 1d) pattern exhibits rhombus symmetry dots, further confirms the single crystalline nature of the primary NWO particles. Elemental mapping of NWO (Figure S1, Supporting Information) shows that Nb, W, and O elements are homogenously distributed.

It is well known that the intrinsic crystalline structure is very important for Li<sup>+</sup> intercalation. The atomic structure of NWO adopting I-4 tetragonal symmetry possesses cornershared MO<sub>6</sub> (M stands for Nb or W atoms distributed statistically) octahedron chains, which can be described in terms of  $4 \times 4 \times \infty$  ReO<sub>3</sub>-type blocks extending over the *ab* plane (Figure 1d). These blocks are joined up with WO3 tetrahedra in the *ab* plane and share the edges of MO<sub>6</sub> octahedra out of the *ab* plane.<sup>[11]</sup> Accordingly, there are nine parallel tunnels spreading along the *c* axis in every block, which intrinsically facilitates the Li<sup>+</sup> diffusion in the lattice. Moreover, these tunnels are also interconnected along the *a* and *b* axes through the tetrahedral hollows formed by the edge-shared MO<sub>6</sub> octahedra, which enables a three-dimensional highway network for ionic diffusion with minimum channel-blocking. Actually, channelblocking issues during cycling dramatically impedes ionic diffusion in many bulk electrode materials with one-dimensional diffusion paths like LiFePO4.<sup>[12]</sup> The three-dimensional tunnel network spreading over NWO structure ensures unobstructed Li<sup>+</sup> ions diffusion even in micro-size particles. For a visualized view of the atomic-scale structure and the tunnels, STEM with high-angle annular dark field detector (STEM-HAADF) was carried out for NWO. Along the [001] projection (Figure 1e), bright spots could be observed at all the cationic sites of the I-4 structure, but the contrast of oxygen atoms is invisible, which is due to the much weaker electron scattering of oxygen compared to







**Figure 1.** a) Schematic illustration of the synthetic procedure of NWO. b) SEM image of the morphology at micrometer-scale. c,d) HR-TEM image and the corresponding SADE patterns of NWO. The planes in both real and reciprocal spaces are labeled. e) Structural illustration of Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub> along the *c* axis and *b* axis. f,g) Aberration-corrected HAADF images of atomic arrangement viewed along the [001] and [0-10] crystallographic directions, respectively. The red circles represent the W atoms at tetrahedral sites and the blue circles stands for the Nb and W atoms distributed at the octahedral sites.

that of Nb and W atoms. Notably, the WO<sub>3</sub> tetrahedral sites, which act as the joints of the blocks, could be clearly recognized by the bright contrasts distributed periodically (marked as red spheres). Moreover, the atomic arrangement viewed along the [0-10] zone axis also accords with the *I*-4 symmetry (Figure 1f). These results firmly demonstrate that the NWO prepared by our solution combustion method is at a high degree of crystallinity without atomic disorders, which ensures the expedite tunnels for fast Li<sup>+</sup> diffusion.

The sharp and well-resolved XRD peaks of NWO further confirms the high crystalline properties resulting from the hightemperature annealing. The Bragg peaks in the XRD patterns could be successfully described with the tetragonal *I*-4 model by Rietveld refinements (**Figure 2**a). The refined lattice constants are a = b = 20.99331 Å, c = 3.82151 Å, which are consistent with the previous results.<sup>[13]</sup> In addition, the successful synthesis of NWO is further supported by Raman spectra (Figure 2b).

Four obvious peaks are observed in the 200–1100 cm<sup>-1</sup> region, corresponding to the features of NWO. Among them, the two strong and broad peaks at  $\approx$ 256.9 and  $\approx$ 631.0 cm<sup>-1</sup> could be assigned to the Nb(W)-O bonds and oxygen-bridged Nb(W)-O-Nb(W), respectively, while the other two peaks at ≈894.5 and  $\approx$ 973.8 cm<sup>-1</sup> could correspond to the WO<sub>6</sub> and NbO<sub>6</sub> octahedra, respectively.<sup>[14]</sup> X-ray photoelectron spectroscopy (XPS) was further employed to study the electronic states of NWO. The Nb 3d spectra (Figure 2c) exhibits typical spin-orbit doublets at 209.7 eV (Nb  $3d_{5/2}$ ) and 207.0 eV (Nb  $3d_{3/2}$ ), which could be assigned to the Nb5+ oxidation state.[15] Additionally, the W 4f spectra (Figure 2d) shows two components at 37.7 and 35.5 eV, which can be distinguished by the splitting orbits of W  $4f_{5/2}$  and W  $4f_{3/2}$ , respectively. The inter-peak separation of 2.2 eV reveals that the W atoms are at +6 valance state.<sup>[16]</sup> Figure 2e compares the tap densities of commercial graphite, commercial TiO<sub>2</sub>, commercial Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and NWO by loading these samples with

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**Figure 2.** a) Rietveld refinement of the XRD patterns for NWO. The raw experimental data are shown with blue crosses and the calculated pattern is shown in orange lines. The black vertical lines stand for the Bragg positions of the *I*-4 space group. The green line depicts the difference of the raw data and the calculated patterns. b) Raman spectra of NWO. c) Nb *3d* XPS spectra and d) W *4f* spectra of NWO. e) The comparison of tap densities: 1) commercial graphite, 2) commercial  $TiO_2$ , 3) commercial Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, 4) NWO.

the same mass in glass tubes (SEM images of all the samples are shown in Figure S2, Supporting Information). It is clearly revealed that NWO possesses a much higher tap density compared with graphite,  $TiO_2$  and  $Li_4Ti_5O_{12}$ , which enables a great prospect of industrial applications dependent on volumetric energy density.

To evaluate Li<sup>+</sup> storage properties of as-prepared NWO samples, various electrochemical measurements were conducted (Figure 3). Figure 3a shows the CV curves of the NWO in the initial four cycles between 1.0 and 3.0 V (vs Li<sup>+</sup>/Li) with a scan rate of 0.1 mV s<sup>-1</sup>. Each CV curve exhibits a couple of weak peaks at  $\approx 2.01/\approx 2.06$  V and a couple of sharp peaks at  $\approx 1.68/\approx 1.83$  V, corresponding to the reduction/oxidation reactions of the  $W^{6+}/W^{5+}$  and  $Nb^{5+}/Nb^{4+}$  redox couples, respectively.<sup>[17]</sup> The broad shoulder peaks in the voltage region of 1.4-1.0 V could be assigned to the further reduction of Nb<sup>4+</sup>/  $Nb^{3+}$  and  $W^{5+}/W^{4+, \left[18\right]}$  Moreover, the small polarization of NWO (0.15 V) implies good high-rate performance of NWO. Figure 3b shows the representative charge/discharge profiles of NWO at 0.5 C (1 C = 0.178 A  $g^{-1}$ , calculated by one electron transfer per transition metal atom). The initial discharge and charge capacities are 249.2 and 220.0 mAh g<sup>-1</sup>, respectively, leading to a high initial coulombic efficiency (CE) of 88.3%. The average lithiation voltage of NWO is about 1.7 V that is far beyond the potential of Li plating, which ensures the intrinsic safety of NWO anode at high rate. Interestingly, voltage profiles after the fifth cycle are almost overlapped, suggesting the excellent electrochemical reversibility. After 200 cycles at 0.5 C, a highly reversible capacity of 215.9 mAh  $g^{-1}$  with 98.1%

capacity retention can be retained (Figure 3c). As expected, the NWO electrode also exhibits an outstanding rate capability, which is obviously superior than that of commercial  $Li_4Ti_5O_{12}$  (Figure 3d). When the current density is stepwise increased from 0.5 C to 1, 2, 5, 10, 20, and 50 C, the NWO electrode delivers high average capacities of 221.3, 201.5, 183.3, 156.2, 134.7, 112.3, and 84.4 mAh g<sup>-1</sup>, respectively. Even at an extremely high current density of 100 C corresponding to a short duration of 24 s charge/discharge process per cycle, a considerable capacity of 57.7 mAh g<sup>-1</sup> can still be maintained. The long-term cycling sustainability has been regarded as a pivotal factor for practical LIB application. At a high current density of 10 C, the NWO electrode remains  $\approx$ 130 mAh g<sup>-1</sup> over 4000 cycles with negligible decay, revealing the excellent reversibility of lithiation/delithiation under high rate condition. Even increasing the loading mass of NWO to 2.7 mg cm<sup>-2</sup>, a stable capacity of 122.3 mAh g<sup>-1</sup> can be retained after 1500 cycles at 10 C (Figure S3, Supporting Information).

The remarkable rate performance of NWO may benefit from the rapid electrode kinetics, which is derived from its three-dimensional open tunnel network. From the GITT result (Figure 3f), apparent Li<sup>+</sup> diffusion coefficients ( $D_{Li^+}$ ) can be obtained (Figure 3g). The value of  $D_{Li^+}$  is affected by the coordination environment of Li<sup>+</sup> insertion, and only a weak bump is observed at about 1.75 V during the discharge process. This result reveals that the Li insertion in NWO may be mainly based on a single-phase solid-solution reaction with minimal phase transformation.  $D_{Li^+}$  of NWO is in the order of  $10^{-10}-10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>, which is distinctly higher than that of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, TiO<sub>2</sub> and TiNb<sub>2</sub>O<sub>7</sub>



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**Figure 3.** a) CV curves of NWO with a scan rate of 0.1 mV s<sup>-1</sup>. b) Galvanostatic charge–discharge profiles of NWO at 0.5 C. c) Cycle performance at 0.5 C. d) Rate performance of NWO and commercial  $Li_4Ti_5O_{12}$  at various current densities. e) Long-term cycling performance of NWO at 10 C. f) GITT curves and g) the calculated apparent  $Li^+$  ions diffusion coefficients from GITT of NWO. h) EIS of the NWO electrode after different cycles.

 $(10^{-12}-10^{-15} \text{ cm}^2 \text{ s}^{-1})$ .<sup>[19]</sup> To gain further insights into the superior electrochemical performance, electrochemical impedance spectroscopy (EIS) of the NWO electrode after different cycles were also conducted (Figure 3h). The compressed semicircle in high-medium frequency region represents the charge transfer resistance ( $R_{ct}$ ), and the slope at low frequency is related to Warburg impedance.<sup>[20]</sup> The  $R_{ct}$  after 50 cycles is slightly larger than that after ten cycles, which is likely due to the self-modification of interface between electrode and electrolyte. From the 50th to 200th cycle, the  $R_{ct}$  values almost remain constant with an incredibly small variation, revealing very stable interface of the NWO electrode with prolonged cycling.

The structural change of NWO within the initial discharge– charge process was studied by using in situ synchrotron highenergy XRD. **Figure 4**a shows the two-dimensional contour plot of the XRD patterns coupled with the corresponding voltage profile. All the diffraction peaks could be identified as the tetragonal *I*-4 phase of NWO, except for the ones appeared at the Bragg positions of face-centered-cubic (fcc)-type  $\gamma$ Fe current collector. From the contour plot, a reversible evolution was observed for all the diffraction peaks of NWO without any break of continuity. In addition, no newly emerged feature was detected throughout the entire discharging and charging process. Two typical groups of peak plots, (2 4 0) and (0 1 1), were presented to detail their smoothly evolving behavior (Figure 4b). Accordingly, as the lithium ions are embedded into the host, a single-phase solid-solution reaction is expected for the present NWO anode material, in contrast to the multiple structural transformations observed in other complex frameworks of niobium tungsten oxides, such as Nb<sub>16</sub>W<sub>5</sub>O<sub>55</sub> and Nb<sub>18</sub>W<sub>16</sub>O<sub>93</sub>.<sup>[10a]</sup> It could be speculated that the lattice strain induced from the structural transitions, which are the major concerns of the niobium tungsten oxides, are reduced significantly in our NWO anode material.

For a more specific view, the lattice parameters at different voltages were extracted from the XRD patterns using Rietveld method.<sup>[21]</sup> As expected, all the XRD patterns could be described well with the tetragonal *I*-4 structure (Figure S4, Supporting Information), which confirms the moderate solid-solution reaction instead of the abrupt structural transition. As shown in







**Figure 4.** a) Contour plot of the in situ XRD patterns for the NWO material along with the corresponding voltage profile. b) Contour plots of the (0 2 4) (left) and (0 1 1) (right) Bragg peaks. c) Lattice evolution of NWO extracted from the in situ XRD patterns. Different regions are highlighted in different background colors, and also depicted in (a) at correlated voltages.

Figure 4c, both *a*- and *c*-axis undergo an expansion at the initial state of discharge ( $I_1$  region), indicating that the *I*-4 framework could tolerate a small amount of Li insertion without altering the electronic and bonding environments. Upon further lithiation, while the c-axis continues to expand steadily, the ab plane exhibits a contraction as discharging from  $\approx$ 1.7 to  $\approx$ 1.3 V ( $I_2$  region), indicating that the Li<sup>+</sup> diffusion path could be along the *c* direction. This anisotropic lattice shrinkage in this stage could be derived from the electrostatic attraction between Li and O ions, accompanied with the reduction of  $W^{6+}/W^{5+}$  and Nb<sup>5+</sup>/Nb<sup>4+</sup> couples observed in the CV curves (Figure 3a). Afterward, the *ab* plane shows another evolutive break, exhibiting a crossover from contraction to expansion as it proceeds toward the end of discharge ( $I_3$  region). This behavior could be related to the further reduction of  $W^{5+}/W^{4+}$  and  $Nb^{4+}/Nb^{3+}$  couples. Just as observed in many layered transition-metal oxides,<sup>[22]</sup> the excess charge of W<sup>4+</sup> and Nb<sup>3+</sup> might be compensated from O<sub>2p</sub> through the highly hybridized W-O and Nb-O channels, so the attraction between Li and O ions in turn weakened upon deep lithiation. The above lattice evolution turns out to be completely reversible, which demonstrates the high reversibility of the multistep  $W^{6+}/W^{5+}/W^{4+}$  and  $Nb^{5+}/Nb^{4+}/Nb^{3+}$  redox reactions. Also, the moderate process of solid-solution reaction, other than abrupt phase transitions, could reduce the lattice strain and thereby internal fracture over cycling, which benefits the long-term performance of the NWO anode material.

To further understand the redox behavior in NWO during lithium insertion/extraction process, in situ XANES

spectroscopy was carried out to track the changes of valence states in Nb and W, as shown in Figure S5, Supporting Information. The Nb K-edge absorption edge, which probes the unoccupied Nb-5p states through 1s-5p excitations, exhibits a gradual shift to the lower energy upon discharging, indicating the continuous reduction of Nb accompanied with lithium insertion. In addition, the pre-edge feature located before the absorption edge arises from the Jahn-Teller distortion induced by the empty  $d^0$  state of Nb<sup>5+</sup>.<sup>[10a]</sup> As the Nb<sup>5+</sup> is reduced and the empty *d* states are occupied during discharging, the intensities of the pre-edge peaks fade gradually, manifesting the inhibited local distortions coordinated with Nb4+ and Nb3+. Meanwhile, this increased symmetric coordination of Nb<sup>4+</sup> and Nb<sup>3+</sup> also gives rise to the sharpened white-line peak at ≈19 007 eV upon deep lithiation, as a result of strengthened resonances of scattered electron by neighboring atoms.<sup>[23]</sup> On the other hand, a similar red-shift in the absorption energy of W  $L_3$ edge is also observed during discharging, which confirms the engagement of W in the redox reactions. Remarkably, all the above changes, including the energy (i.e., electronic structure) and the shape (i.e., local coordinating environment) of the Nb K-edge and W  $L_3$ -edge spectra, exhibit a completely reversible feature upon charging. Accordingly, a highly reversible cationic redox process has been demonstrated, which agrees well with the structural reversibility revealed by the in situ XRD results. Furthermore, the valence state changes of Nb and W could be estimated based on the linear relationships between the edge shifts in energy and the transferred electrons.<sup>[10a,24]</sup> As shown

in Figures S6a,b, Supporting Information, the energy shift ( $\Delta E$ ) of Nb K-edge between the open circuit voltage (OCV) and final discharge states is about 2.4 eV, larger than that between Nb<sup>5+</sup> and Nb<sup>4+</sup> ( $\approx$ 1.9 eV). This result confirms the successive reductions of Nb<sup>5+</sup>/<sup>4+</sup> and Nb<sup>4+/3+</sup> during discharging process. A similar analysis was also performed on the W L<sub>3</sub>-edge (Figures S6c,d), revealing the W<sup>6+/5+</sup> and W<sup>5+/4+</sup> redox couples engaged in the battery reactions. These rich and reversible redox couples underlying the structural stability ensure the fast and endurable Li ion transport and the high performance of NWO electrode.

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We also performed ex situ Raman spectra of the NWO electrode during different charging states to further clarify the mechanism of the remarkable cycling performance (Figure 5a). A weak peak located at ≈339 cm<sup>-1</sup> corresponding to Li–O–M bonds appears during the discharging process and then disappears during the charging process by degrees, indicating the reversible Li<sup>+</sup> intercalation/de-intercalation processes.<sup>[25]</sup> Region 4 corresponding to NbO<sub>6</sub> and WO<sub>6</sub> octahedra are related to the highest oxidation states of metal atoms (Nb<sup>5+</sup> and W<sup>6+</sup>). The peaks in region 4 are weaken gradually and nearly vanish when discharged to 1.0 V, and become evident again when charged to 3.0 V. These results reveal the highly reversible redox reactions of Nb<sup>5+</sup>/Nb<sup>4+</sup>,  $Nb^{3+} \, and \, W^{6+}/W^{5+}, \, \bar{W}^{4+} \, couples.$  The Raman spectrum after one whole cycle is similar with that of the pristine NWO, indicating that the crystal structure of NWO can be retained during cycling. More importantly, no other new peaks are emerged except for the above-mentioned peak 2, and no obvious shift is observed for peak 1 (M–O bonds) and peak 3 (M–O–M bonds) during cycling, confirming the single-phase solid-solution electrochemical mechanism with negligible phase transformation.

To obtain deep insights into the role of the three-dimensional open tunnel network of NWO in the improved rate capability, first-principles calculations were carried out (Figure 5b-i). Clearly, the compound exhibits a layered structure that contains plenty of interconnected tunnel structured cavities in the (001) surface (see in Figure 1b). It is found that Li ion prefers to occupy an off-center site that is coordinated by four interlayer O atoms, as shown in Figure 5g-i. The binding energy (calculated using bulk Li as the reference state) for Li intercalation is -3.01 eV. Three representative diffusion paths including the migration between layers (i.e., along Path I and Path II) and that through a Nb/WO6 layer (Path III) were investigated (Figure 5b,c). The migration barrier, which determines Li<sup>+</sup> diffusivity, depends on the diffusion paths. The calculated results are shown in Figure 5d-f. As shown in Table S4, Supporting Information, the energy barriers for Li<sup>+</sup> ion diffusion along each direction in Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub> (<0.21 eV) are much smaller than that of graphite, anatase  $TiO_2$ ,  $Li_4Ti_5O_{12}$ , and even T-Nb<sub>2</sub>O<sub>5</sub> (a well-recognized anode material shows anomalously fast rate of Li<sup>+</sup> storage), revealing the facile and rapid Li<sup>+</sup> transport features. According to the formula  $D = a^2 v^* \exp(-E_a/k_BT)$ , the diffusion coefficient along each diffusion direction can be evaluated. a,  $v^*$ ,  $E_a$ ,  $k_B$ , and T correspond to the hopping distance between two adjacent sites, hopping frequency (10<sup>13</sup> s<sup>-1</sup>), the largest barrier along each direction, Boltzmann's constant, and the temperature (300 K), respectively. The estimated diffusion coefficients along the three paths are  $1.13 \times 10^{-4}$ ,  $1.95 \times 10^{-4}$ , and  $3.75 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup> in turn, which is even six orders of magnitude higher than the ultrafast sodiation observed in NaZnSb ( $1.28 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ ).<sup>[26]</sup> These results clearly suggest that the specific structure of NWO enables fast Li<sup>+</sup> migration channels spreading over the framework.

The high performance of NWO anodes motivated us to fabricate Li-ion full batteries. Therefore, we prepared LFP/NWO full cells with capacity limited by anode and the electrochemical properties were evaluated (Figure 6). Herein, commercial LiFePO<sub>4</sub> (LFP) was adopted as the cathode due to its high safety feature.<sup>[2a]</sup> The average output voltage of the LFP/NWO full cell is about 1.8 V (Figure 6a), and the fabricated pouch cell can light a LED light with the working voltage of ≈2.0 V. The LFP/NWO battery delivers discharge capacities of 226.9, 198.5, 135.3, 105.8, and 70.3 mAh  $g^{-1}$  at rates of 0.5, 1, 5, 10, and 20 C, respectively (Figure 6b,c). Impressively, when the current density returns to 0.5 C, the capacity recovers to 217.5 mAh g<sup>-1</sup> immediately, revealing the high tolerance against high-rate cycling for the LFP/NWO battery. Figure 6d shows the long-term cycling performance of LFP/NWO battery. Encouragingly, the cell exhibits excellent cycling stability, and still maintains ≈91.1% of its initial capacity after 1000 cycles at the high current density of 10 C. Ragone plots of the NWO electrode and some of the previously reported high-safety anodes (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and TiO<sub>2</sub>) versus the LFP cathode in full cells are summarized in Figure 6e.<sup>[27]</sup> The NWO electrode can exhibit a high energy density of 405.4 Wh kg<sup>-1</sup> at a power density of 162.0 W kg<sup>-1</sup> and an extraordinary power density of 6480 W kg<sup>-1</sup> at an energy density of 126.1 Wh kg<sup>-1</sup>, which are prominent compared with other reported high-safety anodes. Moreover, considering its intrinsic high tap density, the volumetric energy density of NWO electrode is also appreciable. To increase the operating voltage of the full battery, we can also use high-voltage LiNi0.5Mn1.5O4 (LNMO) as the cathode to couple with NWO anode. The as-fabricated LNMO/NWO full cell can output a high average working voltage of 2.95 V with a reversible capacity of 212.4 mAh  $g^{-1}$  at 0.5 C (Figure S7, Supporting Information).

For practical LIB applications, safety performance should be also highly considered. Thermal runaway is one of the most significant safety hazards for LIBs, which is usually triggered by the exothermal reactions between highly reactive electrode materials and electrolytes.<sup>[28]</sup> These issues are even more important when large-scale LIBs are used. Thus, identifying electrode materials with good thermal stability plays an important role in the fabrication of high-safety LIBs. The chemical reactivity of lithiated graphite (LiC<sub>6</sub>) is similar to metallic Li, which may react violently with binders and electrolytes at elevated temperature. Generally, replacing graphite anode as Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> can greatly improve the thermal stability of LIB.<sup>[29]</sup> Therefore, as a powerful competitor to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, investigating the thermal stability of NWO is also necessary. Differential scanning calorimetric (DSC) traces of lithiated Li4Ti5O12 and NWO wet with electrolyte are shown in Figure 6f. Both DSC curves exhibit three exothermic regions, assigned to the decomposition reaction of SEI (solid-electrolyte-interface), lithiated anode materials-electrolyte reduction reaction, and the reaction of lithiated anode material with binder, respectively.<sup>[30]</sup> The total generated heat of lithiated NWO anode (514.1 J  $g^{-1}$ ) is lower than that of lithiated  $Li_4Ti_5O_{12}$  (612.8 J g<sup>-1</sup>), and all three exothermal peaks shift to slightly higher temperature, indicating better thermal







**Figure 5.** a) Ex situ Raman measurements of the NWO electrode during the initial cycle. b–i) Theoretical calculation of Li diffusion in Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub>. b) Top and c) side views for Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub> structure. The NbO<sub>6</sub> octahedra and WO<sub>6</sub>/WO<sub>4</sub> octahedra/tetrahedra are shown in gray and blue polyhedra, respectively. The red arrows indicate possible Li diffusion paths, named as Path I, Path II, and Path III. Calculated minimum energy paths of Li diffusion along Path I (d), Path II (e), and Path III (f) in layered Nb<sub>14</sub>W<sub>3</sub>O<sub>44</sub>. g–i) Corresponding views of diffusion pathways. The black balls indicate Li ions at the most energetically favorable site for Li intercalation. The NbO<sub>6</sub> octahedra and WO<sub>6</sub> octahedra are shown in gray and blue polyhedra, respectively.

stability of NWO. Cycling performance of battery at elevated temperature is also very important for practical LIBs, especially for high-safety applications. As shown in Figure 6g, the NWO half-cell exhibit a high reversible capacity of 138.0 mAh g<sup>-1</sup> after 1000 cycles at 50 °C with the current density of 10 C. Moreover, the discharge capacity of LFP/NWO full cell is as high as

100.5 mAh g<sup>-1</sup> after 1000 cycles at 50 °C. The prominent cycling stability and superior thermal stability demonstrated the feasibility of the LFP/NOW full battery.

In summary, a micro-size  $\rm Nb_{14}W_3O_{44}$  (NWO) adopting I-4 tetragonal symmetry was successfully synthesized by a facile solution combustion method. The three-dimensional open







**Figure 6.** a) Charge–discharge voltage profiles of the NWO anode and LiFePO<sub>4</sub> cathode at 0.5 C (inset: photograph of a LED light powered by the LFP/NWO pouch cell). b) Rate performance and c) galvanostatic charge–discharge profiles of the LFP/NWO full cell at various current rates between 1.0 and 2.5 V. d) Long-term cycling performance of the LFP/NWO full cell at 10 C. e) Ragone plots for the NWO electrode with comparison of previously reported high-safety anode materials (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and TiO<sub>2</sub>) versus the LFP cathode. f) DSC measurements of lithiated NWO and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> g) Cycling performance of the NWO full cell at 50 °C.

tunnel network in NWO can provide expedite Li<sup>+</sup> diffusion pathways and avoid channel blocking effect effectively, which ensures the high-rate performance in micro-size particles. In situ synchrotron high-energy XRD, in situ XANES, and ex situ Raman studies demonstrate that the Li<sup>+</sup> insertion and extraction in NWO is a single-phase solid-solution electrochemical mechanism with highly reversible redox reactions, leading to excellent structural stability during cycling. The as-prepared NWO exhibits remarkable rate capability and extraordinary long-term cycling stability (a high capacity of  $\approx 130$  mAh g<sup>-1</sup> can be maintained at 10 C after 4000 cycles with no decay) without the assistance of nanosizing, coating, and so on, which overcomes the critical barriers of nanosized electrodes. Considering the prominent thermal stability and safety characteristics, our prepared NWO have great promise as ultrahigh-rate and highsafety anode materials for LIBs.

#### **Experimental Section**

Detailed sample synthesis method for NWO, characterizations, theoretical calculations, and electrochemical measurements are presented in Supporting Information.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

anode materials, high-rate electrode materials, high-safety, lithium-ion batteries, niobium tungsten oxides

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