Enhanced lithiation dynamics in nanostructured Nb$_{18}$W$_{16}$O$_{93}$ anodes

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HIGHLIGHTS

- Grain size control of Nb$_{18}$W$_{16}$O$_{93}$ through a simple calcination process.
- Downscaling grains below 100 nm results in 170 mAh/g after 100 cycles.
- Grain boundaries in Nb$_{18}$W$_{16}$O$_{93}$ enable pathways for fast lithium ion diffusion.
- Capacity loss during charge-discharge is due to the redox reaction at 2.1 V.

ABSTRACT

Lithium ion batteries are essential for energy storage in many applications, such as portable electronic devices and electric vehicles. However, charge-discharge rates and cycle life of the current batteries are insufficient to fulfill the targeted requirements of projected future devices, due to the severe limitations of conventional graphite anodes. Niobium tungsten oxides have recently been attracting attention as a new anode material for fast (dis)charging, owing to their stable host structure for lithium intercalation. It was originally believed that nanoscaling and nanostructuring would have a negligible effect on its electrochemical performance. However, the influence of the particle and grain size of niobium tungsten oxide electrodes on its electrochemical behavior is still an open question. This work reports on an investigation of the dependence of the lithiation process on the grain size of Nb$_{18}$W$_{16}$O$_{93}$ anodes down to 60 nm. The results demonstrate that downscaling below 100 nm significantly enhances the lithiation dynamics of niobium tungsten oxide. Furthermore, it suggests that the grain boundaries of Nb$_{18}$W$_{16}$O$_{93}$ have significant influence to the fast lithiation process. It provides a new perspective on the impact of downscaling grains to improve the electrochemical performance of Nb$_{18}$W$_{16}$O$_{93}$ anodes for realizing fast (dis)charging in future energy storage devices.
1. Introduction

Energy storage has been attracting a lot of attention over the past decade, as it is essential for realizing global energy sustainability[1,2]. Energy storage devices such as batteries and supercapacitors play a key role in many applications like portable electronic devices and electric vehicles. Lithium ion batteries (LIBs) are among the most successful device technologies in this field with its high energy density and high efficiency[3–6]. However, LIBs are becoming the bottleneck in technology development, as the current specific capacities of electrodes, charge-discharge rates and cycle life of the battery are insufficient to fulfill the targeted requirements of projected future devices[7–9].

One of the main reasons for the meager rate of development in LIB technology are the severe limitations at high discharge rates of conventional graphite anodes, i.e. increased particle fracture and accelerated lithium dendrite formation, which stimulates capacity degradation, short circuiting and possibly even destruction of the battery in later stages[10–12]. This problem occurs for all low-voltage anode materials as the increasing internal resistance causes an increase of the over-potential, which leads to lithium plating and dendrite formation. New anode materials with higher voltages of the chemical reaction and higher (dis)charge rates are needed for next-generation LIBs[13].

Titanium-based oxides are promising candidates to fulfill those requirements[13–19], as Li4Ti5O12 and TiO2 exhibit working voltages of about 1.55 and 1.8 V[20–22], respectively, which prevents lithium plating and enables high rate lithium intercalation[23]. Niobium based oxides and vanadium based oxides also have comparable working potentials[24–26]. Recent studies have shown that composites of Li4Ti5O12 nanosheets with 3D carbon can reach capacities of 140 mAh g⁻¹ at a rate of 64C[27] and epitaxial Li4Ti5O12 thin films even offer 280 mAh g⁻¹ at a rate of 30 C[28]. Various studies on TiO2 indicate similar improvements: mesoporous yolk–shell anatase TiO2/TiO2(B) microspheres reached capacities of 181 mAh g⁻¹ at a rate of 40C[29] and hollow multi-shelled heterostructured anatase TiO2/TiO2(B) provided capacities of 125 mAh g⁻¹ at a rate of 20 C[30]. However, previous material design strategies exhibit significant disadvantages, as the incorporation of carbon within the composites as well as the mesoporous structure design reduce the volumetric capacity[31].

A recent study has shown that niobium tungsten oxides (NbWO) exhibit enhanced lithium diffusion rates and electronic properties as compared to TiO2 and Li4Ti5O12[34]. The lithium diffusion coefficients of Li6Nb15W10O53 (1.1 × 10⁻¹³ m² s⁻¹) and Li6Nb16W5O35 (1.7 × 10⁻¹³ m² s⁻¹) are several orders of magnitude higher than Li4.8Ti5O12 (10⁻¹⁶ m² s⁻¹) and Li2TiO2 (10⁻¹⁵ m² s⁻¹), which indicates that lithium transport in niobium tungsten oxides is remarkably faster than in titanium oxides[34]. Furthermore, both the tetragonal NbWO phases (Nb6W2O55[34], Nb14W2O44[35]) as well as the distorted tetragonal tungsten bronze NbWO phases (Nb6W2O47[36], Nb18W12O53[33,34]) exhibit exceptional electrochemical performance with charge-discharge rate up to 20 C over hundreds of cycles.

The high lithium ion diffusion coefficient has been attributed to the presence of one-dimensional channels within the host crystal structure[34], as illustrated in Fig. 1(a). Three types of one-dimensional channels can be distinguished: a pentagonal channel, a square channel and a triangular channel. The lithiation process, during which lithium ions are inserted into the structure, has been proposed to follow the order from first the largest channel (pentagonal), then the intermediate channel (square) and finally the smallest channel (triangular), as shown in Fig. 1 (b). During this charge discharge procedure the original Nb16W10O53 phase transforms consecutively into Li16Nb15W10O53, then Li22Nb16W12O63 and ultimately Li20Nb14W12O63, by subsequently filling each type of channel[33]. It was also concluded in the same study that nanoscaling and nanostructuring of the NbWO anode host material would not lead to significant further improvement of its electrochemical performance and it was thus suggested to focus further research on identifying better host structures for lithium intercalation with enhanced diffusivity for the counter electrode. In contrast, other recent studies have indicated that one-dimensional NbWO nanofibers exhibit enhanced electrochemical performance as compared to their powder NbWO[33,35,36], which would suggest that nanostructuring is a relevant approach to improve the electrochemical performance of NbWO. Furthermore, the relationship between the particle and grain size with the electrochemical properties have been well studied in other systems such as Ti based oxides, but not in niobium tungsten oxide[37]. Therefore, the influence of downscaling grain sizes within NbWO electrodes on its electrochemical behavior still remained a debated question and a detailed study on the impact of grain size on the electrochemical performance of Nb6W2O53 is required.

Here, we studied the debated relationship between NbWO grain size and its corresponding electrochemical behavior in more detail, and
report our findings on the effect of downsizing of NbWO anodes. We successfully synthesized tungsten bronze \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powders with different grain sizes (60, 100 and 130 nm) using a calcination method with varying calcination times. The average grain sizes were determined by X-ray diffraction (XRD), while the particle sizes were obtained from scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. Cyclic voltammetry and charge-discharge cycling were used to determine the relationship between grain size, insertion reaction and electrochemical performance. Comparison of the electrochemical performance of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) with different grain sizes indicates that smaller \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) grains exhibited significantly enhanced cycling and rate performance, which leads to the conclusion that the grain size is a key parameter for achieving enhanced lithiation dynamics in downscaled \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) electrodes.

2. Experimental

Control of the grain sizes in the \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powders was achieved through synthesis by a calcination process adopted from a NbWO phase diagram study in the 1960s [38]. Niobium pentoxide (\( \text{Nb}_2\text{O}_5 \), 99.9%, Alfa Aesar) and tungsten trioxide (\( \text{WO}_3 \), 99.8%, Alfa Aesar) in a molar ratio 9:16 were ground by ball milling in ethanol for 24 h. Subsequently, the obtained precursor mixture was calcined at 1473 K for 2, 20 or 72 h, respectively, in order to obtain powders consisting of particles with different grain sizes. All further investigations and comparisons are all based on these three sample types [48].

The crystal structure of the \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powders was studied by X-ray diffraction (PANalytical X'Pert PRO diffractometer with Cu Kα radiation and 1/8 slit, in steps of 0.0016° and 10.2 s/step). The morphology, particle size and elemental distribution of pristine samples, as well as the morphology and the SEI layer of the cycled samples, were determined by scanning electron microscopy (SEM, Zeiss Merlin HRSEM) and energy dispersive X-ray spectrometry (EDX, Oxford Instruments; detector: X-Max 80 mm² silicon drift detector (SDD) with a large area; software: Aztec 3.3 SP1). The crystal lattice and grain boundary formation were measured by Scanning Transmission Electron Microscopy (STEM, Titan Themis TEM with C.EOS probe and image aberration corrector operated at 200 keV) for \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powder with a grain size of 130 nm. The Nb:W ratio was measured by X-ray fluorescence (XRF, Bruker S8 Tiger WDXRF with a Rhodium X-ray Tube).

Electrodes were made by mixing the active \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) phase, conductive carbon and binder material (mass ratio of 8:1:1) with mortar and pestle. The mixture was pasted on a Cu foil with about 2–5 mg cm⁻² loading within an area of 1 cm². The active \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) material and conductive carbon (acetylene black, Super P) were beforehand ground in an agate mortar and pestle by hand for 30 min. The binder material, polyvinylidene difluoride (PVDF, Mw 27,500, Sigma-Aldrich) was dissolved in N-methyl pyrrolidone (NMP, 99.9%, Sigma-Aldrich) to a concentration 0.05 g ml⁻¹ by stirring for 48 h. Subsequently, the mixture of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powder and conductive carbon was dispersed in the PVDF solution in an ultrasonic bath for 20 min. The electrode fabrication process was performed in a fume hood as \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powder and conductive carbon consist of nanoparticles and NMP is a hazardous organic solvent.

All electrochemical experiments were conducted in Li-cells (ECC-ref) in which the electrodes consisting of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) paste on Cu foil were measured in a half-cell configuration against a lithium metal (99.9%, Sigma-Aldrich) anode. A standard liquid electrolyte was used in all the experiments containing 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate/dimethyl carbonate (EC/DMC, Sigma-Aldrich, battery grade), while as separator a standard 18 mm diameter and 1 mm thick glass fiber material (ECCI-01-0012-B-L) was applied. The electrochemical measurements were performed at room temperature in a galvanostat/potentiostat (VMP-300, BioLogic) with EC-Lab software and the reported potentials are relative to Li⁺/Li⁺.

3. Results and discussion

The crystalline phase of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles with different calcination times was investigated by XRD. Fig. 2(a) shows the X-ray diffractograms of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles calcined for 2, 20 and 72 h. All reflections can be indexed assuming the distorted tetragonal \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) tungsten bronze crystal structure with space group Pbam (JCPDS card: No. 01-075-0561) [32]. The results indicate that the calcination time does not affect the crystallographic phase of the \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) powders. The variation in grain sizes for \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) samples with different calcination times were determined from the width of the (001) reflection using the Scherrer equation [39].

\[
D_{\text{hkl}} = \frac{k\lambda}{\beta \cos \theta}
\]

where \( D_{\text{hkl}} \) is an estimate of the grain size; \( k \) is the shape factor; \( \lambda \) is the X-ray wavelength; \( \beta \) is the full width of the peak at half maximum (FWHM); and \( \theta \) is the diffraction angle. The FWHM values were obtained from a Gaussian fit of the (001) peaks, as illustrated in Fig. 2(b). The (001) peak was selected since almost all other peaks consist of two overlapping reflections. The FWHM of the (001) peaks of powders calcined for 2, 20 and 72 h are 1.35° ± 0.010°, 0.82° ± 0.001° and 0.66° ± 0.0013°, respectively. This corresponds to grain sizes of 60, 100 and 130 nm, respectively, suggesting that extending the calcination time yields larger \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) domains.

The SEM images of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles in Fig. 3(a)-(c) illustrate the increasing particle size (0.5 μm–1.5 μm) with increasing calcination time, which differ significantly from grain size calculations based on the XRD results. The existence of these small primary grains in these secondary particles are proven by the grain boundary STEM images (Fig. 4(d) and (e)). As can be seen in Fig. 3(d)-(f), the morphology of \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles is cylindrical independent of calcination time, and the level of aggregation is similar as in previous reported work [34]. The degree of agglomeration appears not to be affected by the calcination time.

The morphology of the NbWO electrodes was also characterized after 100 charge-discharge cycles under 1 C in the voltage range 1.2–3.0 V, showing the particles embedded in conductive carbon and binder matrix, see Fig. 3(g)-(i) and Fig. S1. The morphology and size of the particles remained the same, suggesting that volume expansion during charge-discharge cycling was limited, which may be due to the well-defined crystal structure containing lithiation channels that allow Li insertion/extraction with minimal strain on the surrounding lattice. EDX mapping indicates that Nb, W and O elements are homogeneously distributed within the cylindrical \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles, see Fig. S2(a)-(e). The atomic Nb:W ratio in the powders is 17.4:16 (as measured by XRF), as shown in Table S1, close to the theoretical 18:16 atomic ratio in the \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) crystal structure.

In order to study the crystal lattice and the grain boundary formation within the NbWO particles, STEM analysis was performed on a specimen extracted perpendicular to the length of a 72 h-calcined \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) particles, as shown in Fig. 4(a). Atomic resolution STEM imaging clearly shows the in-plane \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) crystal lattice, as shown in Fig. 4(c), matching to the (001) Miller plane of the tungsten bronze structure. The particle indeed consists of smaller grains, which are all aligned with the c-axis along the length of the cylindrical shape. However, the individual grains within the particle are rotated in-plane (a, b-axes) with respect to each other which results in the formation of grain boundaries, Fig. 4(d) and (e). The angle between the upper (010) plane and the boundary in Fig. 4(e) is around 64°, which indicates that this grain boundary is not a twinning plane. Furthermore, as illustrated in Fig. 4(d) and Fig. S3(b), there are more grain boundary images that show that internal grain boundaries between in-plane rotated grains and between \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) grains and reconstructed \( \text{Nb}_3\text{W}_{16}\text{O}_{93} \) grains are common. Those grain boundaries...
boundaries are formed by the local reconstruction of the lattices of the adjacent Nb$_{18}$W$_{16}$O$_{93}$ grains, and they exhibit a width of about 2 nm. These specific reconstructed grain boundaries are expected to play a crucial role in the fast lithium diffusion processes within these cylindrical particles. Electron diffraction analysis of this specimen, Fig. 4(b), shows the presence of two preferred orientations with the typical 3.67 nm lattice spacing for the [010] direction (standard values are listed in Table S2). The electron diffraction pattern of a single grain area in the Nb$_{18}$W$_{16}$O$_{93}$ slice in Fig. S3(a) clearly shows that the (010) reflection only appears in one direction, which further proves that two preferred orientations are present in Fig. 4(b). This is also observed in the STEM image, Fig. 4(e), which shows the in-plane alignment of the grains with a 90° rotation between them.

The specific surface areas of the NbWO samples were investigated by

Fig. 2. (a) X-ray diffraction patterns of Nb$_{18}$W$_{16}$O$_{93}$ powders calcined for 2 h, 20 h and 72 h. (b) FHWM determination of the (001) reflection of Nb$_{18}$W$_{16}$O$_{93}$ powders made with different calcination times.

Fig. 3. (a)–(c) Top view SEM images of Nb$_{18}$W$_{16}$O$_{93}$ particles after calcination of 2, 20 and 72 h, respectively. (d)–(f) Zoomed in SEM images of morphology of Nb$_{18}$W$_{16}$O$_{93}$ particles after calcination of 2, 20 and 72 h, respectively. (g)–(i) SEM images of mixed electrode pastes containing Nb$_{18}$W$_{16}$O$_{93}$ particles after calcination of 2, 20 and 72 h, as well as conductive carbon and binder after cycling in a half-cell configuration.
Fig. 4. (a) Schematic representation of the specimen extraction by focused-ion-beam perpendicular to the length of a 130 nm size Nb$_{18}$W$_{16}$O$_{93}$ grain; (b) Electron diffraction pattern of the Nb$_{18}$W$_{16}$O$_{93}$ slice; (c) STEM image of the in-plane (a,b-axes) Nb$_{18}$W$_{16}$O$_{93}$ crystal lattice; (d)-(e) STEM images of the grain boundary formation.

applying Brunauer–Emmett–Teller (BET) analysis on nitrogen sorption data of NbWO powders with different grain sizes. As can be seen in Fig. S4(a), Nb$_{18}$W$_{16}$O$_{93}$ particles with smaller grain sizes adsorbed more nitrogen, which means that they exhibit a larger specific surface area. The specific surface areas of 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders were 0.9945 ± 0.0044 m$^2$ g$^{-1}$, 0.7028 ± 0.0069 m$^2$ g$^{-1}$ and 0.5226 ± 0.0081 m$^2$ g$^{-1}$, respectively, as shown in Fig. S4(b) and Table S3. These results indicate that the particle size of Nb$_{18}$W$_{16}$O$_{93}$ increases along with the grain size, which is in agreement with the SEM images in Fig. 3. Thus, longer calcination times do not only increase the grain size, but also the particle size of Nb$_{18}$W$_{16}$O$_{93}$. The specific surface area is roughly proportional to 1/d, where d is the diameter of the cylindrical Nb$_{18}$W$_{16}$O$_{93}$ particles. However, both SEM and BET analysis indicate that the size of the particles should be in the micrometer range, due to the fact that the particles of Nb$_{18}$W$_{16}$O$_{93}$ are typically polycrystalline, and each particle consists of multiple grains. It can thus be concluded that Nb$_{18}$W$_{16}$O$_{93}$ particles were synthesized with similar morphologies, but different grain and particle sizes.

Electrochemical measurements were performed to determine the relationship between the Nb$_{18}$W$_{16}$O$_{93}$ grain size and the corresponding electrochemical behavior. The initial charge-discharge cycling experiments were done under 1 C in the voltage range 1.0–3.0 V, as shown in Fig. S5. The half cells exhibited a large capacity drop between 20 and 40 cycles. The charge-discharge curves suggest that the Nb$_{18}$W$_{16}$O$_{93}$ host structure either degraded or underwent a specific phase change between the 21st and 51st cycle, as evidenced by the disappearance of the plateau at 2.1 V. Therefore, we limited the voltage range for further electrochemical analysis to 1.2–3.0 V, and prolonged cycling demonstrated that the plateau at 2.1 V was still present after 100 cycles (Fig. S6), which indicates that the Nb$_{18}$W$_{16}$O$_{93}$ host structure was unaffected in this voltage range. Although similar charge-discharge curves with well-defined plateaus can be observed for smaller (2 h and 20 h-calcined) Nb$_{18}$W$_{16}$O$_{93}$ particles (Fig. S6(a)-(b)), this is not the case for large (72 h-calcined) particles (Fig. S6(c)). This could be explained by the fact that Nb$_{18}$W$_{16}$O$_{93}$ with larger grain sizes exhibit a lower concentration of grain boundaries which act as main pathways for fast lithium ion diffusion [40]. Such lower lithium ion diffusivity results in a larger internal resistance, which prevents the 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders to exhibit a clear voltage plateau and leads to reduced electrochemical performance. Furthermore, we calculated the voltage biases for 2 h and 20 h-calcined samples at the 2.1 V plateau [44]. For the 2 h sample, the 2.1 V plateau voltage biases at the 1st, 21st, 51st and 100th cycle were 0.086, 0.082, 0.096 and 0.105 V, respectively. For the 20 h sample, the 2.1 V plateau voltage biases at the 1st, 21st, 51st and 100th cycle were 0.09, 0.096, 0.106 and 0.114 V, respectively. In both samples the voltage biases increased with cycle number. Smaller Nb$_{18}$W$_{16}$O$_{93}$ grains showed less bias, which can be related with lower internal resistance.

Rate performance analysis showed that clear voltage plateaus remained present (Fig. S6(d)-(e)) for the lowest C-rates (1C, 2C and 5C), i.e. the lowest currents. At 20C rate the voltage plateau disappeared for 20 h-calcined sample, similar to the behavior of the largest particles (72 h-calcined sample) at lower C-rates (Fig. S6(f)). Interestingly, the smallest particles (2 h-calcined sample) still exhibited a clear voltage plateau up to 20C, demonstrating that nanostructuring of Nb$_{18}$W$_{16}$O$_{93}$ particles allows enhanced lithiation dynamics and enables faster electrochemical performance as Li anode in a battery. However, all three cases showed a gradual increase in the potential difference between the charge and discharge plateaus suggesting an increasing internal resistance of these three test devices due to the formation of the SEI layer.

The overall cycle life and rate performance of Nb$_{18}$W$_{16}$O$_{93}$ powders with different grain sizes are shown in Fig. 5(a)-(b). The cycle life measurements at 1C (150 mA g$^{-1}$) [27] showed limited capacity loss over 100 cycles and the capacity retentions under these test conditions were 86.3%, 84.8% and 75.7% for the 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ particles, respectively, indicating that smaller particles have a better cycling ability. A higher capacity retention of about 94% was achieved upon cycling at higher current densities, as illustrated for 15 C in Fig. S7. This result is comparable with the work of Griffith et al. (95% capacity retention after 200 cycles at 10 C) [34]. The origin of this
Fig. 5. (a) Cycle life of discharge capacity of 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders over the course of 100 charge-discharge cycles (1.2–3.0 V). (b) Rate dependent discharge capacity of 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders under 1C, 2C, 5C and 20C. (c)-(e) Cyclic voltammetry (1.2–3.0 V, scan rate 0.1 mV s$^{-1}$) data of 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders before and after 100 charge-discharge cycles.
behavior is the reduced degree of lithiation in Nb$_{18}$W$_{16}$O$_{93}$ at such high current densities, which causes less degradation of the crystal structure during extensive charge-discharge cycling. The cycling stability was studied in more detail at lower current densities, at which rates maximum lithium storage capacity can be achieved. The specific capacity of 2 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ particles remained 170 mAh g$^{-1}$ after 100 cycles at 1 C, while a reduced capacity of about 110 mAh g$^{-1}$ (i.e., 68%) was achieved under 20 C. On the other hand, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ only had 49% and 0% capacity retention at 20 C, respectively. Hence, smaller Nb$_{18}$W$_{16}$O$_{93}$ particles exhibit a significantly higher capacity retention under high current cycling than the larger ones.

The superior performance of smaller grains may be caused by their larger specific surface area [41, 42], shorter lithium ion diffusion paths within the grains and higher concentration of grain boundaries which act as fast lithium ion pathways [40]. As discussed above, smaller grains have a larger specific surface area resulting in larger pseudocapacity, which can be a major contribution to the capacity at high rates. For example, CuCo$_2$S$_4$@N/S-doped graphene composite was reported as an anode material in which the surface contributed for 50% to the total capacity [43]. The large specific surface area of the material provided a high concentration of active sites for the lithiation process. Furthermore, fast lithium ion diffusion along internal boundaries was also reported by Tang et al. [47] for glass-ceramic-like vanadate cathodes, which consisted of a secondary phase inside a low-temperature hydrate, allowing stable charge-discharge at 4000 mA g$^{-1}$ (about 15 C).

Cyclic voltammetry (CV) analysis of the different Nb$_{18}$W$_{16}$O$_{93}$ powders showed clear peaks (Fig. 5(c)-(e)), in good agreement with the proposed lithiation processes within the crystal lattice (Fig. 1(b)). Two major peaks at 2.1 and 1.7 V can be observed in the CV curves, which are related to the chemical reactions of niobium [45] and tungsten, respectively, while a hint of a third peak is noticeable at 1.4 V. These three peaks can be associated with the three step lithiation process, in which one chemical intercalation reaction occurs per type of channel (pentagonal, square, triangular). Starting the discharge procedure at 3.0 V the Nb$_{18}$W$_{16}$O$_{93}$ phase transforms into Li$_{13}$Nb$_{18}$W$_{16}$O$_{93}$ at 2.0 V, then into Li$_{21}$Nb$_{18}$W$_{16}$O$_{93}$ at 1.5 V, and ultimately into Li$_{35}$Nb$_{18}$W$_{16}$O$_{93}$ at 1.2 V. CV analysis showed significant differences between the different grain sizes. Firstly, the CV data of the Nb$_{18}$W$_{16}$O$_{93}$ sample with a grain size of 130 nm showed a less distinct peak at 2.1 V, which indicates that a less well-defined chemical reaction at 2.1 V occurs in these larger grains. As discussed above, this could originate from the lower concentration of grain boundaries limiting the lithiation process as well as the reduced contact area with the surrounding conductive carbon increasing the internal resistance limiting its electrochemical performance. Secondly, comparison of CV data before and after cycling shows that the capacity loss was mainly caused by the vanishing of the peak at 2.1 V. Comparison of the CV data of different samples also indicates that

![Fig. 6. (a)-(c) Cyclic Voltammetry at different rates (0.1 mV s$^{-1}$ to 2 mV s$^{-1}$) for 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powders; (d) Calculated pseudocapacity ratio obtained by Dunn’s method.](image-url)
the vanishing chemical reaction at 2.1 V was alleviated by reducing the size of the Nb$_{18}$W$_{16}$O$_{93}$ grains. Thus, it can be concluded that downsizing the grain and particle size of Nb$_{18}$W$_{16}$O$_{93}$ anodes leads to a more stable lithium intercalation at 2.1 V.

To study the variation in pseudocapacitance contribution for Nb$_{18}$W$_{16}$O$_{93}$ powders with different grain sizes, CV measurements were performed at different rates. As can be seen in Fig. 6(a)-(c), the difference between the voltage potentials of the redox peaks is increasing for higher CV rates and larger Nb$_{18}$W$_{16}$O$_{93}$ grains. This indicates that the internal resistance of the anode is higher when the grain size of the Nb$_{18}$W$_{16}$O$_{93}$ electrode material is larger. To obtain more insight, Dunn’s method [48] was used to calculate the pseudocapacitance ratio for different CV rates:

$$i(v) = k_1 v + k_2 v^{1/2}$$

which can be transformed into:

$$i(v)/v^{1/2} = k_1 v^{1/2} + k_2$$

where $i(v)$ is the current at voltage $V$ in the CV curve; $v$ is the rate of CV; $k_1$ is the current contributed by surface chemical reaction (related to pseudocapacitance); $k_2 v^{1/2}$ is the current contributed by diffusion process (related to intercalation capacity). Thus, the surface capacity contribution can be quantified by calculating the slope of this linear curve.

In principle, a large grain will exhibit a low pseudocapacitance ratio because its specific surface area is low. However, the pseudocapacitance ratio will increase if the rate of CV is increased because a faster electron transport will make the lithium diffusion to become the limiting process within the battery. This trend can be observed in Fig. 6(d). Moreover, the capacity retention at 15 C (94%, 200 cycles) is much higher than at 1 C (84.8%, 100 cycles) for 20 h-calcined material, which may be due to an increase of capacitive contribution at higher current densities. However, the pseudocapacitance ratio of 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powder increases faster than the other powders with smaller grains. The grain size of 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$ powder is too large to enable full lithiation under the fast CV rate of 2 mV s$^{-1}$, which is demonstrated by the incomplete reduction peak in Fig. 6(c). For all samples the pseudocapacitance contribution for a sweep rate of 0.5 mV s$^{-1}$ (50.0%, 45.6%, 38.0% for respectively 2 h, 20 h and 72 h-calcined Nb$_{18}$W$_{16}$O$_{93}$) is higher than in nano-sized TiO$_2$ (14.6% for 30 nm particle size) [48]. This large pseudocapacitance ratio at high sweep rate suggests that the Nb$_{18}$W$_{16}$O$_{93}$ grain boundaries enable high rate performance through lithium ion intercalation pseudocapacitance [49], due to the presence of crystalline reconstructed grain boundaries instead of defective or amorphous phases.

Furthermore, we compared the peak current with square root sweep rate [46] and used the Randles–Sevick equation to calculate the lithium ion diffusion coefficients at different redox peaks for 2 h, 20 h and 72 h calcined Nb$_{18}$W$_{16}$O$_{93}$. The Randles–Sevick equation clarifies the relationship between the peak current and CV sweep rate, which is:

$$i_{p} = (2.69 \times 10^{6}) n^{1/2} S D_{li}^{1/2} C_{li}^{1/2} v^{1/2}$$

where $i_{p}$ is the peak current (A), $n$ the charge-transfer number, $S$ the contact area between Nb$_{18}$W$_{16}$O$_{93}$ and electrolyte, $C_{li}$ the concentration of lithium ions in the electrode, $v$ the potential scan rate (V/s).

As shown in Fig. S8 and Table S4, the Li$^+$ diffusion coefficient of Nb$_{18}$W$_{16}$O$_{93}$ can reach a value of 3.24 $\times$ 10$^{-12}$ cm$^2$ s$^{-1}$ (charging peak at 2.1 V, 2 h calcined sample). And from 2 h calcined sample to 72 h calcined sample, all peaks show decreased lithium ion diffusion coefficients. We also made a comparison between our calculated values and other works, as shown in Table S5. It shows that Nb$_{18}$W$_{16}$O$_{93}$ has a large lithium ion diffusion coefficient compared with other high rate anodes. When focusing on the electrochemical performance of our Nb$_{18}$W$_{16}$O$_{93}$ in comparison to other niobium-based electrodes (Table S6), a high rate performance was achieved due to the fast lithium ion diffusion in our nanostructured anode material.

4. Conclusions

The grain size of Nb$_{18}$W$_{16}$O$_{93}$ anodes was successfully controlled in order to determine the debated relationship between grain/particle size and its corresponding lithiation process. Comparison of the electrochemical performance of Nb$_{18}$W$_{16}$O$_{93}$ with different grain sizes indicates that smaller Nb$_{18}$W$_{16}$O$_{93}$ grains exhibited significantly enhanced cycling and rate performance, which indicates that the grain size is still a key parameter for achieving enhanced lithiation dynamics in nanostructured Nb$_{18}$W$_{16}$O$_{93}$ anodes when downsizing below approximately 100 nm. The superior lithiation performance is mainly due to shorter lithium ion diffusion paths within the grains and higher concentration of grain boundaries as fast lithium ion pathways [50]. The original study by Griffith et al. on this material showed also good capacity retention at high C rate using large particles (10–30 μm) of Nb$_{18}$W$_{16}$O$_{93}$ [34], which could be also using high concentration of grain boundaries for fast lithiation. Here it was shown that the grains are aligned with the c-axis along the length of the cylindrical shaped particles, but rotated in-plane (a, b-axes) with respect to each other resulting in ~2 nm wide grain boundaries formed by local reconstruction of the adjacent Nb$_{18}$W$_{16}$O$_{93}$ grains. These specific reconstructed grain boundaries are expected to play a crucial role in the fast lithium diffusion processes as well as enhanced lithium storage within these cylindrical particles.

Finally, the observed degradation of the chemical reaction at 2.1 V is most likely responsible for the observed capacity degradation. In previous work on a Nb$_{18}$W$_{16}$O$_{93}$ nanofiber, ex-situ XPS at different potential states showed that the chemical reaction around 2 V could be attributed to the Nb$^{5+}$ – Nb$^{4+}$ transition, and the chemical reaction at around 1.6 V to W$^{6+}$ – W$^{5+}$ [33]. Thus, we believe that further studies on the degradation mechanism is important and they should be focused on the chemical reaction at 2.1 V, that could be Nb$^{5+}$ – Nb$^{4+}$ as suggested in the above study. In order to improve the cycling stability of the NbWO anode material, we suggest that further studies should focus on improving the stability and reversibility of the electrode reaction by compositional and dimensional modifications.

CRediT authorship contribution statement

**Rui Xia**: Conceptualization, Investigation, Writing - original draft.

**Congli Sun**: Investigation, Supervision. **Yang Wang**: Investigation.

**Daniel Cunha**: Investigation, Software. **Haoyang Peng**: Investigation, Visualization. **Kangning Zhao**: Supervision. **Mark Huijben**: Supervision, Writing - review & editing. **Johan E. ten Elshof**: Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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