Facile formation of tetragonal-Nb$_2$O$_5$ microspheres for high-rate and stable lithium storage with high areal capacity

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Niobium pentoxide (Nb$_2$O$_5$) has attracted great attention as an anode for lithium-ion battery, which is attributed to the high-rate and good stability performances. In this work, TT-, T-, M-, and H-Nb$_2$O$_5$ microspheres were synthesized by a facile one-step thermal oxidation method. Ion and electron transport properties of Nb$_2$O$_5$ with different phases were investigated by both electrochemical analyses and density functional theoretical calculations. Without nanostructuring and carbon modification, the tetragonal Nb$_2$O$_5$ (M-Nb$_2$O$_5$) displays preferable rate capability (121 mAh g$^{-1}$ at 5 A g$^{-1}$), enhanced reversible capacity (165 mAh g$^{-1}$ at 0.2 A g$^{-1}$) and better cycling stability (82.3% capacity retention after 1000 cycles) when compared with TT-, T-, and H-Nb$_2$O$_5$. Electrochemical analyses further reveal the diffusion-controlled Li$^+$ intercalation kinetics and in-situ X-ray diffraction analysis indicates superior structural stability upon Li$^+$ intercalation/deintercalation. Benefiting from the intrinsic fast ion/electron transport, a high areal capacity of 2.24 mAh cm$^{-2}$ is obtained even at an ultrahigh mass loading of 22.51 mg cm$^{-2}$. This work can promote the development of Nb$_2$O$_5$ materials for high areal capacity and stable lithium storage towards practical applications.

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1. Introduction

Nowadays, electrochemical energy storage has found broad applications in smart grid, electric vehicles and portable electronics [1-4]. Although lithium-ion batteries (LIBs) and supercapacitors (SCs) have already achieved commercialization owing to the superior energy density and preferable power density, respectively [5-8], devices that have a balanced energy and power density are still in shortage. On the one hand, LIBs are limited by the slow Li$^+$ diffusion in electrode materials [9,10]. On the other hand, the non-faradaic reaction at the electrode/electrolyte interface hinders the energy density of SCs [11-13]. Therefore, it is of practical significance to develop new-generation electrode materials with a balanced energy/power density [14,15].

Niobium pentoxide (Nb$_2$O$_5$) has been regarded as a potential anode for LIBs due to the prominent pseudocapacitive behavior and excellent rate capability [16-19]. Nb$_2$O$_5$ possesses the theoretical capacity of 200 mAh g$^{-1}$ which is higher than the representative anode material Li$_4$Ti$_5$O$_12$. Nb$_2$O$_5$ works at the voltage range of 1.0 to 2.0 V versus Li/Li$_x$, during which potential range, the formation of solid electrolyte interface film (SEI) and lithium dendrite could be efficiently avoided [20,21]. To date, most researches focus on T-Nb$_2$O$_5$ (orthorhombic, pbam) [22], a typical intercalation pseudocapacitive material, though there are many other polymorphic forms of Nb$_2$O$_5$ including a-Nb$_2$O$_5$ (amorphous), TT-Nb$_2$O$_5$ (pseudohexagonal, PE) [23], M-Nb$_2$O$_5$ (tetragonal, I4/mmm) [24,25] and H-Nb$_2$O$_5$ (monoclinic, P2/m) [26] based on the crystallization temperature [27]. Among them, the intercalation pseudocapacitance of T-Nb$_2$O$_5$ (Fig. S1b online) can immensely enhance its rate capability on the premise of maintaining capacity [28-30]. Liu and co-workers [20] demonstrated the unique Li$^+$ diffusing topological path in T-Nb$_2$O$_5$ from the atomic arrangement, which contributed to a direct Li$^+$ transport between bridging sites with very low steric hindrance. The TT-Nb$_2$O$_5$ (Fig. S1a online) polymorph is deemed as an incompletely crystallized T-polymorph, which contains impurities, or vacancies in the crystal texture [31]. Kumagai and co-workers [32,33] demonstrated that the M-Nb$_2$O$_5$ (Fig. S1c online) was favorable for the reversible Li$^+$ insertion due to the high diffusion coefficient and ordered NbO$_6$ octahedra arrangement, but M-Nb$_2$O$_5$ was hard to prepare due to the strict synthesis condition (at higher...
temperature but for shorter oxidation time. H-Nb$_2$O$_5$ (Fig. S1d online) is the most stable phase due to the highest crystallization temperature over 1000 °C, which displays higher initial capacity but poorer rate performance [34–36].

Recently, Nb$_2$O$_5$-based materials have been widely investigated for LIBs and SCs, but the intrinsic drawback of low electrical conductivity ($\approx$3.4 × 10$^{-6}$ S cm$^{-1}$ at 300 K) hinders its practical applications in large-scale energy storage systems [8,37]. To solve this issue, efforts have been directed to integrate various carbon materials with Nb$_2$O$_5$ nanostructures, such as Nb$_2$O$_5$/graphite [38], Nb$_2$O$_5$/mesocarbon microbeads [39], Nb$_2$O$_5@$carbon cloth [40] and Nb$_2$O$_5$/carbon nanotubes [41,42], where carbon was used as electron transport framework to enhance the electronic conductivity. Recently, Duan and co-workers [43] developed a three-dimensional holey graphene framework as the conductive scaffold for T-Nb$_2$O$_5$ to realize fast ion and electron transport, achieving outstanding rate capability at a high mass loading. However, in general carbon modification and nanostructure are always accompanied with higher specific surface area, leading to a low tap density [44]. Consequently, low tap density materials are hard to realize good cycling stability at a high mass loading and so for achieving high areal capacity, which is crucial for practical applications [45,46]. This is due to the fact that electronic mobility and structural stability are generally hindered with the increased mass loading [47]. Therefore, it is of great significance to develop unmodified materials which possess intrinsic good electron/ion transport properties to realize both cycling stability and high areal capacity.

Herein, TT-, T-, M- and H-Nb$_2$O$_5$ microspheres were synthesized by a facile one-step thermal oxidation method. The results clearly show that M-Nb$_2$O$_5$ displays superior rate capability, higher reversible capacity and better cycling stability than TT-, T-, and H-Nb$_2$O$_5$. Electrochemical analyses, density functional theory (DFT) calculations and in-situ XRD analysis demonstrate that M-Nb$_2$O$_5$ exhibits mainly diffusion-controlled Li$^+$ intercalation and the smallest band gap, thus displaying the fastest ion and electron transports. Consequently, without carbon modification and nanostructuring, the as-prepared M-Nb$_2$O$_5$ microsphere based LIB anode, benefiting from the intrinsic fast ion and electron transport properties, realizes a high areal capacity at an ultrahigh mass loading.

2. Materials and methods

2.1. Material synthesis

The four crystallographic Nb$_2$O$_5$ microspheres were synthesized by a facile and efficient one-step thermal oxidation treatment. First, 200 mg Nb powder was uniformly scattered on a porcelain plate and put it into the heating zone of the tube furnace. Then, the system was sealed and argon gas was purged for 30 min (gas flow-rate $f(\text{Ar}) = 25$ sccm, sccm: standard milliliters per minute) to create a pure Ar atmosphere. After that, the temperature of the furnace was raised to a specified temperature (500–1000 °C) in the Ar atmosphere with a heat rate of 10 °C min$^{-1}$. When rising to the aimed temperature, Ar and O$_2$ gas ($f(\text{O}_2) = f(\text{Ar}) = 25$ sccm) was purged together to start the oxidation process. The oxidation process lasted for 1 h to obtain various crystallographic Nb$_2$O$_5$ microspheres. Afterwards, the O$_2$ gas supply was terminated and the furnace was cooled to room temperature under a flow Ar atmosphere.

2.2. Structural characterization

The crystallographic information of Nb$_2$O$_5$ microspheres were investigated with a Bruker D8 Discover X-ray diffractometer with Cu K$\alpha$ radiation source. Scanning electron microscopy (SEM) images were received by a JEOL-7100F microscope. Transmission electron microscopy (TEM) measurements were tested on a JEOL JEM-2100F STEM/EDS microscope with the accelerating voltage of 200 kV. Thermogravimetric and differential scanning calorimetry (TG-DSC) analyses were employed by a Netzsch STA 449C analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out by an Escalab 250Xi instrument with Al K$\alpha$ radiation. Raman spectra were collected by a Renishaw IN Via micro-Raman spectroscopy system. For in-situ XRD measurement, the battery system was assembled by a mold where the electrode was covered by an X-ray-apparent beryllium sheet. The in-situ XRD signals were acquired by the planar detector in a still mode during the discharge–charge process, and patterns were collected in every 2 min.

2.3. Electrochemical characterization

The electrodes with an ordinary mass loading ($=3.6$ mg cm$^{-2}$) were produced by casting process. Firstly, a homogenous ink was prepared and composed of active materials, acetylene black and carboxymethyl cellulose binder with the mass ratio 7:2:1. After that, the ink was casted on copper foil and dried at 70 °C overnight, and punched into round sheets with a diameter of 10 mm. The electrodes with high mass loading were produced by a rolling process. The mass ratio of active materials, acetylene black and polytetrafluoroethylene binder was also 7:2:1. CR2016-type button batteries were assembled with the lithium foil ($\phi 16 \times 0.6$ mm) as the counter electrode in a glove box under pure Ar atmosphere. Celgard 2500 microporous membranes were employed as separators. The electrolyte was composed of 1 mol L$^{-1}$ LiPF$_6$ dissolved in ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate (1:1:1, v:v:v). The cells were aged for 12 h before testing to ensure the thorough infiltration of the electrolyte into the electrode. The electrochemical performances were tested on a multi-channel battery testing system (LAND CT2001A). The galvanostatic charge/discharge measurements were carried out at the potential range of 1.3–3.0 V versus Li$^+$/Li. Cyclic voltammetry (1.3–3.0 V) and electrochemical impedance spectra (EIS) were tested using an electrochemical workstation (CHI 760E).

2.4. Theoretical calculation

DFT was employed to calculate the band structures of various Nb$_2$O$_5$ phases. The calculations were carried out by the Vienna Ab-initio Simulation Package (VASP), performed with Perdew-Burke-Ernzeh (PBE) generalized gradient approximation (GGA) functional. For the geometry optimization of different Nb$_2$O$_5$ models, the k-point separations in Brillouin zone was 0.04 Å$^{-1}$ and the plane-wave cut-off energy was 500 eV. The self-consistent field (SCF) energy convergence was $1 \times 10^{-5}$ eV atom$^{-1}$ and the lattice force threshold value was 0.02 eV Å$^{-1}$. For the calculation of band structure, the specific k-path with 16 points in every segment for each Nb$_2$O$_5$ model was set, as shown in Fig. S8 (online).

3. Results and discussion

3.1. Structural characterization

TG-DSC analysis was carried out to explore the oxidation process and the phase transition of Nb powder precursor (Fig. S2 online). From the TG-DSC curves, a weight gain at around 300 °C is observed, which can be attributed to the oxidation of Nb powder. A sharp exothermic peak accompanied with a rapid weight increase at around 500 °C is attributed to the phase transition from
an uncharacterized niobium pentoxide hydrate to Nb$_2$O$_5$ crystal (pseudohexagonal) [48]. The weight increase ends at around 600 °C with an increment of 35 wt%. No obvious weight gain or crystallization peaks are observed again even when the temperature increases from 600 to 1000 °C, during which the crystal structure changes from pseudohexagonal to monoclinic. The XRD patterns of evolved phases (Fig. S3 online) indicate that the phase transition of Nb$_2$O$_5$ is highly dependent on the calcination temperature. A pure TT-Nb$_2$O$_5$ was obtained while annealing at 500 °C, with all the characteristic peaks well matched with the pseudohexagonal phase (JCPDS No. 00-028-0317, Fig. 1a) [23]. While heated at 600 °C, all the characteristic diffraction peaks could be indexed to the orthorhombic phase (JCPDS No. 00-030-0873, Fig. 1b) [22], demonstrating that TT-Nb$_2$O$_5$ had successfully transformed to T-Nb$_2$O$_5$. When the heating temperature was set at 700 to 800 °C, several peaks with 2θ at 22°–28°, 32°, 38.8° and 47.6° emerged, indicating that the T-phase was converting into the M-phase. Further lifting the temperature up to 900 °C led to the formation of pure M-Nb$_2$O$_5$ (JCPDS No. 01-072-1484, Fig. 1c) [24]. While the sample was heated to 1000 °C, it shows the pure monoclinic phase (JCPDS No. 01-071-0005, Fig. 1d) [26] which is the most thermodynamically stable phase [21].

The morphological evolution of the as-synthesized samples was clearly revealed by SEM and TEM images in Fig. 2. The Nb powder precursors display as microspheres with the diameter of 1–2 μm. A few tiny particles can be observed on the surface, which indicates the formation of oxidized niobium due to oxidation in the air (as shown in Fig. S4 online). After the thermal treatment, nano-sized Nb$_2$O$_5$ particles formed and further aggregated to large-sized particles. All the Nb$_2$O$_5$ samples with different phases exhibit as microspheres which are composed of nanoparticles at 100–300 nm (Fig. 2a, d, g and j) and nanoparticle size increases at higher heating temperature (Fig. 2g and j). The high-resolution TEM (HRTEM) results and the selected area electron diffraction (SAED) patterns could clarify more morphological information of crystalline Nb$_2$O$_5$. For the sample annealed at 500 °C, Fig. 2b shows the lattice spacing of 3.1 and 3.9 Å, relating to the (1 0 0) and (0 0 1) planes of TT-Nb$_2$O$_5$, respectively. The corresponding SAED pattern in Fig. 2c further reveals the polycrystalline nature of TT-Nb$_2$O$_5$, with two diffraction rings indexed to (1 0 0) and (0 0 1) crystal planes of pseudohexagonal phase. The HRTEM results in Fig. 2e of Nb$_2$O$_5$ sample that was annealed at 600 °C show the interlayer spacing of 3.1 Å, which is identified to the plane (1 8 0) of T-Nb$_2$O$_5$, while the corresponding SAED pattern in Fig. 2f reveals the diffraction rings indexed to (1 8 0), (1 8 1), (0 0 2) and (1 8 2) lattice planes of orthorhombic phase. In the HRTEM image of sample annealed at 900 °C (Fig. 2h), the measured interstitial void of 3.7 Å could be matched to the (1 0 1) crystal plane of M-Nb$_2$O$_5$. The corresponding SAED pattern (Fig. 2i) reveals hexagonal symmetry, which is typical for I4/mmm space group indicating a single crystalline nature. Moreover, the diffraction spots are indexed to (1 0 1), (4 3 1) and (7 6 1) crystal planes of tetragonal phase. The image of sample annealed at 1000 °C (Fig. 2k) demonstrates an interlayer spacing of 3.7 Å, corresponding to (1 1 0) planes of H-Nb$_2$O$_5$, while the corresponding SAED pattern (Fig. 2l) reveals the diffraction spots indexed to (1 1 0), (T 0 5), (T 0 1) and (0 2 0) lattice planes of monoclinic phase. Above all, the crystal phase of Nb$_2$O$_5$ sample gradually transforms as the temperature increases.

![Fig. 1.](Fig. 1. (Color online) High resolution XRD patterns of the products by oxidizing the Nb powder precursor at (a) 500, (b) 600, (c) 900, and (d) 1000 °C.)
The surface valance states of the TT-, T-, M- and H-Nb₂O₅ samples were investigated by XPS measurements. Nb, O, and C can be found in the four samples according to the wide survey XPS spectra (Fig. S5a online). The small C 1s peaks are corresponding to the introduced carbon during testing. The high-resolution Nb 3d XPS spectra are all dominated by the two bands of Nb 3d₅/₂ and Nb 3d₃/₂ situated at around 207 and 210 eV, referring to the typical bands for Nb⁵⁺ in Nb₂O₅ (Fig. S5b online). Fig. S5c (online) shows the high-resolution O 1s XPS spectra, with the sharp peak located at around 530.3 eV and the lower peak at around 531.3 eV being assigned to the O 1s of O²⁻ in Nb-oxides and the surface oxygen, respectively [49]. With the increase of the annealing temperature, the XPS peaks of Nb and O slightly shift toward high binding energy direction, which is due to the reduction of oxygen vacancies in these samples [50]. The Raman spectra of TT-Nb₂O₅ and T-Nb₂O₅ are similar with a high-wavenumber band group (m_Hi) ranging from 570 to 770 cm⁻¹ and a mid-wavenumber band group (m_Mid) ranging from 180 to 360 cm⁻¹ being observed, which is consistent with the previous studies on vibrational band groups of T-Nb₂O₅ [20,51]. In the Raman results of M-Nb₂O₅ and H-Nb₂O₅, the strong peaks observed in the range 200–300, 600–700 and 950–1050 cm⁻¹ are assigned to the T₂u, Eₙ and A₁g modes, respectively. These results are in agreement with previous reports on Nb₂O₅ single crystals and nanocrystalline powder [52–54]. To sum up, the results demonstrate that the pure-phase TT-, T-, M-, H-Nb₂O₅ samples were obtained.

### 3.2. Electrochemical performance

Furthermore, the as-prepared TT-, T-, M- and H-Nb₂O₅ samples were used as anode materials for LIBs to investigate the Li⁺ intercalation behavior. The first four CV curves (Fig. 3a–d) of all samples overlap well, indicating good reversibility. TT-Nb₂O₅ and T-Nb₂O₅ show broad Li⁺ intercalation/deintercalation peaks, which exhibit obviously different behaviors from M-Nb₂O₅ and H-Nb₂O₅. The main peaks in four samples are corresponding to Li⁺ insertion...
and extraction in the Nb$_2$O$_5$ lattices. The charge-discharge curves of the as-prepared TT-, T-, M- and H-Nb$_2$O$_5$ samples at varied current densities are also recorded (Fig. 3e–h). Smooth sloping voltage curves for TT-Nb$_2$O$_5$ and T-Nb$_2$O$_5$ and obvious plateau for M-Nb$_2$O$_5$ and H-Nb$_2$O$_5$ are observed, in consistent with the CV results. When cycled at the relatively low current density of 0.1 A g$^{-1}$, M-Nb$_2$O$_5$ and H-Nb$_2$O$_5$ present a discharge capacity of 162.3 and 151.8 mAh g$^{-1}$, respectively, much higher than TT-Nb$_2$O$_5$ (112.2 mAh g$^{-1}$) and T-Nb$_2$O$_5$ (117.3 mAh g$^{-1}$). However, when increasing the current density to 5 A g$^{-1}$, the discharge capacities of TT-Nb$_2$O$_5$, T-Nb$_2$O$_5$ and H-Nb$_2$O$_5$ all sharply decrease to a low level (19.3, 33.2 and 67.8 mAh g$^{-1}$, respectively), whereas M-Nb$_2$O$_5$ still maintains a discharge capacity as high as 121.6 mAh g$^{-1}$. The capacity retentions for TT-, T-, M- and H-Nb$_2$O$_5$ samples are summarized in a table inset in the figure (the $i$ values are for the cathodic processes are 162, 157, 148, 140, 130 and 121 mAh g$^{-1}$ when cycled at 0.1, 0.2, 0.5, 1, 2 and 5 A g$^{-1}$, respectively. More importantly, the discharge capacity of M-Nb$_2$O$_5$ returns to as high as 164.7 mAh g$^{-1}$ when recovering the current density to 0.1 A g$^{-1}$ after testing at the abovementioned different rates, indicating extraordinary structural stability of M-Nb$_2$O$_5$. Moreover, long-term galvanostatic charge/discharge measurements of the TT-, T-, M- and H-Nb$_2$O$_5$ samples were tested at 0.2 A g$^{-1}$ (Fig. 3j). Obviously, M-Nb$_2$O$_5$ exhibits a stable specific discharge capacity of 163 mAh g$^{-1}$ which is superior to that of TT-, T- and H-Nb$_2$O$_5$ (110, 105 and 154 mAh g$^{-1}$, respectively). After performing for 1000 cycles, M-Nb$_2$O$_5$ exhibits a higher capacity retention of 82.3% than TT-Nb$_2$O$_5$ (66.8%), T-Nb$_2$O$_5$ (80.4%) and H-Nb$_2$O$_5$ (65.3%), confirming the excellent cycling stability of M-Nb$_2$O$_5$. Additionally, the initial Coulombic efficiency of M-Nb$_2$O$_5$ is 91.4%, higher than TT-Nb$_2$O$_5$ (74.7%), T-Nb$_2$O$_5$ (72.2%) and H-Nb$_2$O$_5$ (88.1%), indicating a high reversibility at the first lithiation/delithiation process. Therefore, M-Nb$_2$O$_5$ sample displays outstanding rate capability and excellent cycling stability, which shows great prospect for ultrafast charging/discharging and long lifespan LIBs.

In addition, to evaluate the Li$^+$ intercalation kinetics of as-prepared TT-, T-, M- and H-Nb$_2$O$_5$ samples, CV measurements were performed at varied scan rates from 0.1 to 1.0 mV s$^{-1}$ (Fig. S6a–d online). According to the power relationship between the current (i), mA; and the sweep rate (v, mV s$^{-1}$): $i = av^n$, the charge storage controlled by diffusion ($b = 0.5$) or surface-confined processes ($b = 1$) can be reflected by the b-value, and the b-value is dependent on the slop value of the log-log plots [56,57]. As shown in Fig. S6e (online), the kinetics of Nb$_2$O$_5$ at various crystalline structures are compared, and the b-values of various crystalline Nb$_2$O$_5$ are summarized in a table inset in the figure (the b1 values are related to the anodic peaks and the b2 values are for the cathodic peaks). The b-values of T-Nb$_2$O$_5$ are very close to 1, manifesting that the kinetics of Li$^+$ migration is controlled by surface-confined process and exhibits capacitive behavior, which is coincident with the previous reports by Dunn and co-workers [57]. In contrast, the b-values of M-Nb$_2$O$_5$ are close to 0.5, demonstrating that the kinetics of Li$^+$ transport in M-Nb$_2$O$_5$ is limited by diffusion process. Furthermore, EIS was employed to understand the charge-transfer behavior and the lithium-ion diffusion processes in TT-, T-, M- and H-Nb$_2$O$_5$ pristine electrode materials. It is clear that M-Nb$_2$O$_5$ shows the smallest charge-transfer resistance among them (Fig. S7a online), indicating fast electronic mobility.
plots are presented in Fig. S7b (online). It is clear that M-Nb$_2$O$_5$ exhibits a slope value of 7.08, much lower than TT-Nb$_2$O$_5$ (726.81), T-Nb$_2$O$_5$ (662.21) and H-Nb$_2$O$_5$ (16.22). As the square of the slope value (stand for Warburg factor) has an inverse relationship with Li$^+$ diffusion coefficient, it indicates that the M-Nb$_2$O$_5$ exhibits most efficient diffusion kinetics among four samples. To confirm the superior electronic conductivity of M-Nb$_2$O$_5$ than other Nb$_2$O$_5$ phases, DFT calculations were carried out to obtain the band structures of various Nb$_2$O$_5$ phases (Fig. 4). The corresponding high symmetrical k-paths are presented in Fig. S8 (online). As a result, the TT-, T-, M-, and H-Nb$_2$O$_5$ are semiconductors with obvious indirect band gaps, 2.0, 2.2, 1.7 and 2.8 eV, respectively. The band gap of M-Nb$_2$O$_5$ is the smallest, which means the transfer of electrons from valence band to conduction band is the easiest.

3.3. Lithium storage mechanism

In order to reveal the lithium storage mechanism in M-Nb$_2$O$_5$, in-situ XRD technique was employed to investigate the structural evolution during Li$^+$ intercalation/deintercalation processes (Figs. 5 and S9 (online)). At the initial voltage, the diffraction peaks situated at 23.6°, 32.0° and 38.7° are identified to the (1 0 1), (4 3 1) and (7 0 1) planes, respectively. During discharging process, all these diffraction peaks gradually shift to lower angles, indicating an expanded lattice spacing due to the Li$^+$ intercalation, with the formation of Li$_x$Nb$_2$O$_5$. Conversely, these diffraction peaks shift back to high diffraction angles during the following charging process, which is in accordance with the lithium extraction process accompanied by Li$_x$Nb$_2$O$_5$ to Nb$_2$O$_5$. There are no new phase generated during the Li$^+$ insertion/extraction processes, demonstrating the insertion-type Li$^+$ storage mechanism, which is favorable for efficient lithium storage in the electrode materials [58]. The shift behavior of XRD bands during the next three cycles are similar to that in the first cycle, indicating that M-Nb$_2$O$_5$ has an excellent structural stability upon the Li$^+$ insertion/extraction processes.

3.4. Performance at high mass loading

To investigate the superiority of M-Nb$_2$O$_5$ as the LIB anode material, M-Nb$_2$O$_5$ electrode with the mass loadings ranging from 12.12 to 22.51 mg cm$^{-2}$ were prepared by controlling the thickness with the rolling technique. Fig. 6a displays the achieved areal capacity and gravimetric capacity of the M-Nb$_2$O$_5$ electrodes at varied mass loadings, with the galvanostatic charge/discharge measurements carried out at a current density of 0.2 A g$^{-1}$. A high areal capacity of 1.22 mAh cm$^{-2}$ is obtained at the mass loading of 12.12 mg cm$^{-2}$, with the capacity retention of 95.1% after 100 cycles. As the mass loading of electrodes increases from 13.50 to 14.24, 15.41, 16.82, 18.90, 19.65 and 22.51 mg cm$^{-2}$, the corresponding reversible areal capacities are 1.38, 1.45, 1.57, 1.73, 1.94, 1.99 and 2.24 mAh cm$^{-2}$, and the capacity retention after 100 cycles are 94.9%, 91.7%, 90.4%, 87.3%, 90.2%, 87.9% and 81.7%, respectively. Clearly, the cycling stability becomes worse when the mass loading increases. The corresponding charge–discharge profiles at gradient mass loadings are displayed in Fig. 6b. Consistent charge and discharge platforms are observed at all these mass loadings, indicating that the Li$^+$ intercalation behavior is not influenced by varying mass loadings. The relationships of areal capacity and gravimetric capacity with gradient mass loadings are displayed in Fig. 6c. Obviously, the initial reversible gravimetric capacities at different mass loadings ranging from 12.12 to 22.51 mg cm$^{-2}$ are almost the same (approximately 144 mAh g$^{-1}$), and the areal
capacities display a linear increase with the gradient mass loadings. These properties indicate that similar Li$^+$ intercalation behaviors occur in most of the electrode materials, which is on account of the intrinsic ultrafast ion and electron transport properties of M-Nb$_2$O$_5$. The EIS results of pristine electrodes at gradient mass loadings are presented at Fig. 6d. The electrode with the mass loading of 12.12 mg cm$^{-2}$ shows the lowest charge-transfer resistance among them, while the others show almost the same interfacial charge-transfer impedance with the mass loadings of 13.50, 14.24, 15.27 and 18.90 mg cm$^{-2}$. The lithium-ion diffusion only displays a slight change with the augment in mass loading, which is due to the decreased conductivity with the increase in the electrode thickness. Additionally, as shown in the Fig. S10 (online), the electrode materials at a mass loading of 12.58 mg cm$^{-2}$ show unchanged morphology after 100 cycles, demonstrating good structural and cycling stability of M-Nb$_2$O$_5$ even at a high mass loading. Based on above results, it can be deduced that M-Nb$_2$O$_5$ represents a promising anode material for LIBs, which can exhibit both high-areal capacity and long-cycle lifespan even at a high mass loading.
4. Conclusions

In summary, TT-, T-, M- and H-Nb$_2$O$_5$ microspheres were synthesized by a facile one-step thermal oxidation method. When employed as anodes for LIBs, the as-prepared M-Nb$_2$O$_5$ exhibits superior rate capability, higher reversible capacity (163 mAh g$^{-1}$ at 0.2 A g$^{-1}$), and stable cycling performance (82.3% capacity retention after 1000 cycles at 0.2 A g$^{-1}$) compared with TT-, T-, and H-Nb$_2$O$_5$. Electrochemical analyses show that M-Nb$_2$O$_5$ displays diffusion-controlled fast Li$^+$ intercalation kinetics. In-situ XRD analysis confirms the robust structure of M-Nb$_2$O$_5$ upon the Li$^+$ insertion/extraction processes. Additionally, due to the intrinsic fast ion and electron transport properties of M-Nb$_2$O$_5$, high mass loading electrodes ranging from 12.12 to 22.51 mg cm$^{-2}$ are obtained, leading to a high areal capacity (over 2.24 mAh cm$^{-2}$ at 22.51 mg cm$^{-2}$) with good cycling stability. This work reveals the application prospect of M-Nb$_2$O$_5$ as a high areal capacity anode for LIBs.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Liqiang Mai and Qi Li were in charge of this scientific research project, and the leaders of actual coordination of contributions. Zhiqian Hu performed all the experiments and the data analyses as well as wrote the manuscript. Yan Zhao and Qiu He performed the density functional theory calculations. Ziang Liu and Xiong Liu contributed to the conception of the study and revised the manuscript. Mingsheng Qin, Bo Wen and Wenchao Shi helped discuss and revise the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.04.011.

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