Electronic Supplementary Information

TiNb₆O₁₇: a new electrode material for lithium-ion batteries

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Experimental

TiNb₆O₁₇ was prepared by a one-step solid-state reaction from TiO₂ (Sigma–Aldrich, 99.9%) and Nb₂O₅ (Sigma–Aldrich, 99.9%) with a predetermined molar ratio of Nb : Ti = 6 : 1. These precursors were mixed and milled by a ball-milling machine (SPEX 8000M) for 4 h, and finally calcined at 1200 °C for 4 h in a muffle furnace in air. As a comparison, $Ti_2Nb_{10}O_{29}$ was also synthesized by the same process except that the ratio of Nb : Ti = 5 : 1.

Detailed crystal structures of TiNb₆O₁₇ and Ti₂Nb₁₀O₂₉ were identified using X-ray diffractions (XRD) combined with Rietveld refinements. XRD patterns for the refinements were recorded in an angle interval of 5–130° (2θ) with a step width of 0.03° and a counting time of 8 s per step using an X-ray diffractometer (Bruker D8, Germany) with a monochromatic Cu K α radiation ($\lambda = 0.1506$ nm). *Ex-situ* XRD patterns were collected between 10° to 70° (2θ) at a scanning speed of 1° min⁻¹. The refinements were carried out using the GSAS program with the EXPGUI interface.^{S1,S2} During these refinements, the following instrumental and structural parameters were refined: background parameters, zero-shift, unit cell parameters, profile parameters, atomic fractional coordinates and atomic isotropic displacement parameters. The site occupancies were constrained to the designed chemical formulas. The site occupancy of O^{2–} ions was fixed to be unity. Morphologies, particle sizes and microstructures were examined using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and a transmission electron microscopy (TEM, JEOL JEM-2100, Japan). Nitrogen adsorption–desorption isotherms at 77 K were obtained in a surface area analyser (Quantachrome NOVA 2200e,

USA). Specific surface areas were derived based on the Brunauer–Emmett–Teller (BET) model.

Electrochemical performances were examined by the tests of CR2016 coin cells assembled in an argon-filled glove box (Mbraum, Unilab, Germany). In these cells, pure Li foils were used as counter and reference electrodes, microporous polypropylene films (Celgard 2400, Celgard LLC., USA) as separators, and a mixture of ethylene carbonate, dimethyl carbonate and diethylene carbonate (1 : 1 : 1 by weight) containing 1 M LiPF₆ (DAN VEC) as electrolyte. Their corresponding working electrodes were fabricated by a slurry-coating procedure. The slurries contained 65 wt% active materials (TiNb₆O₁₇ or Ti₂Nb₁₀O₂₉), 25 wt% super P[®] conductive carbon (TIMCAL Ltd.) and 10 wt% polyvinylidene fluoride (PVDF, Sigma–Aldrich) in N-methylpyrrolidone (NMP, Sigma–Aldrich). After homogeneously blended, these slurries were uniformly coated on Cu plates. The coated plates were then dried in a vacuum oven at 120 °C for 10 h and finally roller-pressed by a rolling machine to form the working electrodes.

Galvanostatic discharge–charge tests were conducted using a multi-channel battery testing system (LANHE CT2001A, China) with a cut-off potential of 3.0–0.8 V vs. Li/Li⁺. All discharge/charge rates were denoted using C-rate where 396 mA g⁻¹ was assigned to the current density of 1 C. To prepare the electrodes for the *ex-situ* XRD experiments, the coin cells at different states of charge were disassembled, and then the working electrodes were washed by dimethyl carbonate for three times and dried at 80 °C. Cyclic voltammetry (CV) measurements were performed using an electrochemical workstation (Zahner zennium, Kronach, Germany).

- [S1] A. C. Larson and R. B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, L.A.N.L, Los Alamos, 1994.
- [S2] B. H. Toby, J. Appl. Cryst., 2001, 34, 210.



Fig. S1 Crystal structure of Ti₂Nb₁₀O₂₉ exhibiting the m \times n $\times \infty$ (m = 4 and n = 3) ReO₃-type

blocks.







Fig. S2 HRTEM images (a, b) and SAED pattern (c) of TiNb₆O₁₇, and HRTEM images (d, e) and

SAED pattern (f) of Ti₂Nb₁₀O₂₉.

Fig. S2 shows the HRTEM images and SAED patterns of TiNb₆O₁₇ and Ti₂Nb₁₀O₂₉. As can be seen in Fig. S2a, the atomic layers in TiNb₆O₁₇ are positioned in an orderly and repeated pattern. If combining a thick and two thin white lines (the atomic layers indicated by the arrows) as a unit, the layers can be considered as the orderly arrangement of the unit. The interval between the units is 1.03 nm, which is equal to a half of the lattice parameter *c* (Table 1 in the manuscript). Similar layer arrangement was observed in TiNb₂O₇ with a similar Wadsley-Roth shear structure (Fig. 2e in Ref. 17, X. Lu, Z. L. Jian, Z. Fang, L. Gu, Y. S. Hu, W. Chen, Z. X. Wang and L. Q. Chen, *Energy Environ. Sci.*, 2011, **4**, 2638. Please note that its interval of 1.03 nm is equal to a half of the lattice parameter *a* of TiNb₂O₇). As shown in Fig. 1a in our manuscript, *c* is parallel to the width direction of the block (*i.e.*, n direction). Thus, the unit can reflect the characteristics of the width of the block, and the three atomic layers in the unit can correspond to the width of the block (n=3). In addition, from Fig. S2a and Fig. S2d, both TiNb₆O₁₇ and Ti₂Nb₁₀O₂₉ have the same units. Therefore, the width of the block (n=3) was not changed.

Furthermore, as can be seen in Fig. S2b, the atomic layers in $TiNb_6O_{17}$ are also positioned in an orderly and repeated pattern. If combining three white lines (the atomic layers indicated by the arrows) as a unit, the layers can be considered as the orderly arrangement of the unit. The interval between the units is 1.55 nm, which is equal to the lattice parameter *a* (Table 1). As shown in Fig. 1a, *a* is not parallel to or perpendicular to the length/width direction of the block (*i.e.*, m/n direction). Thus, the unit can reflect the characteristics of the block (including length and width). In addition, from Fig. S2b and Fig. S2e, both $TiNb_6O_{17}$ and $Ti_2Nb_{10}O_{29}$ have the same units. Therefore, not only the width (n=3) but also the length (m=4) of the block were not changed.

In addition, the SAED patterns of both samples (Fig. S2c and Fig. S2f) can be indexed as the same $Ti_2Nb_{10}O_{29}$ -type crystal structures. Therefore, it can be concluded that the block structure was not changed and that the two samples have similar crystal structures.





Fig. S3 FESEM images of (a) $TiNb_6O_{17}$ and (b) $Ti_2Nb_{10}O_{29}$.



Fig. S4 Ex-situ XRD patterns of (a) TiNb₆O₁₇ and (b) Ti₂Nb₁₀O₂₉ electrodes after (i) as-fabricated, (ii)

first-discharged to 0.8 V vs. Li/Li⁺, (iii) first-charged to 3 V vs. Li/Li⁺, and (iv) charged to 3 V vs. Li/Li⁺ in the 10th cycle. Identical discharge–charge rates were used.