Supplementary Materials for

Micrometer-scale single crystal particle of niobium titanium oxide enabling Ah laminated pouch cell with superior fast-charging capability

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1. Experimental Section

Material preparation: TiO_2 and Nb_2O_5 powers were used as precursors to fabricate the single crystal $TiNb_2O_7$ particle via a feasible one-step solid-state reaction. After fully mixed, the precursors were annealed under 1100 °C for 12 h in a muffle furnace.

Material characterization: The crystal structure information of TiNb₂O₇ was collected by employing X-ray diffraction (XRD, PANalytical B. V. instrument) with Cu K α 1 radiation (λ =1.5406 Å,) at 40 kV with 40 mA. The elemental components and chemical states of TiNb₂O₇ under various state of charge were identified by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W) with A1 K α radiation. The microstructure of the TiNb₂O₇ was characterized by the transmission electron microscope (TEM, FEI Talos f200x).

Electrodes preparation: The TiNb₂O₇ electrode for coin cell assembly consisted of 80 wt% active materials, 10 wt% polyvinylidenefluoride (PVDF) binder and 10 wt% acetylene black conductive additives. It was fabricated using a slurry approach with 1-Methyl-2-pyrrolidinone as the solvent for dispersion and Cu foil as the current collector. The typical mass loading of the electrode was ~3 mg cm⁻². The TiNb₂O₇ electrode for the *operando* XRD measurement used stainless steel grid as current collector with same electrode components. LiFePO₄ electrode for full type coin cell was composed of 90

wt% LiFePO₄ active material, 5 wt% PVDF binder, and 5 wt% acetylene black conductive additive with a mass loading of ~5 mg cm⁻². The TiNb₂O₇ electrode for pouch cell consisted of 92 wt% active materials, 5 wt% PVDF binder, and 3 wt% acetylene black conductive additive. The mass loading of the electrode reached ~17 mg cm⁻² (double side electrode) and the compaction density was 2.8 g cm⁻³. The LiCoO₂ electrode for pouch cell consisted of 95 wt% active material, 3 wt% PVDF binder, and 2 wt% acetylene black. It possessed a mass loading of ~24 mg cm⁻² (double side electrode) and a compaction density of 3.0 g cm⁻³. The pouch cell comprised stacked layers of cathode, separator, and anode, all of which were packaged by aluminumplastic film. After the electrolyte filling, the pouch cell was vacuumed before electrochemical test.

Electrochemical analysis: All the CR2032 coin-type cell and laminated pouch cell were fabricated in an Ar-filled Mikrouna glovebox (Shanghai, China). Polypropylene membrane was used as separator. Lithium metal was used as the counter electrode in half cell. 1 M LiPF₆ was dissolved in the mixed solvent of dimethyl carbonate, ethylene carbonate, and ethyl methyl carbonate (volume ratio of 1:1:1) for the electrolyte. The galvanostatic charge/discharge measurement was carried out on the LAND battery test systems at room temperature. The cut-off voltage ranges for TiNb₂O₇||Li metal cell was 1–3 V. The cut-off voltage ranges for LiFePO₄||TiNb₂O₇ and LiCoO₂||TiNb₂O₇ cells were 1.0-2.5 V and 1.0-3.0 V, respectively. The electrochemical impedance spectroscopy (EIS) and cyclic voltammogram (CV) measurements were carried out on the BioLogic VMP-300 electrochemical workstation. Multi-sweep CV measurements of TiNb₂O₇ electrode were conducted at 0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 mV s⁻¹, respectively. The frequency range was set as 100 mHz -100 KHz with an amplitude of 10 mV for EIS measurement. The GITT measurement was conducted on LAND battery test systems employing the galvanostatic current density of 0.2 C with a current pulse duration of 20 min and then relax 20 min.

2. Supplementary Figures



Fig. S1 First-cycle charge/discharge profile of the micrometer-scale single crystalline $TiNb_2O_7$ at 0.2 *C*.



Fig. S2 Nitrogen adsorption-desorption isotherm curves of the MSC-TiNb₂O₇.

The surface area of the MSC-TiNb₂O₇ was evaluated by the nitrogen physisorption isotherms measurement and a low Brunauer Emmett Teller (BET) surface area of 1.17 m² g⁻¹ was shown, which could suppress the side reactions between the MSC-TiNb₂O₇ and electrolytes.



Fig. S3 The value of median voltage difference for charge/discharge profiles at various current densities.



Fig. S4 Rate performance comparison between the MSC-TiNb $_2O_7$ and previous TiNb $_2O_7$ -based materials.



Fig. S5 (a) CV curves of TiNb₂O₇ electrode at different sweep rate from 0.1 mV s⁻¹ to 1.1 mV s⁻¹ and (b) the corresponding log i vs. log v plots. (c) CV curve with the pseudocapacitive fraction at the scan rate of 1.1 mV s⁻¹. (d) The percent of pseudocapacitive contribution and diffusion contribution at different scan rates.



Fig. S6 The rate performance of (a) the LiFePO₄||TiNb₂O₇ full cell and (b) the corresponding charge/discharge curves at different current densities. (c) The cycling performance of LiFePO₄||TiNb₂O₇ full cell at 2 *C* and (d) the corresponding charge/discharge curves.



Fig. S7 Schematic diagram of the structure for the $LiCoO_2 ||TiNb_2O_7$ pouch cell.



Fig. S8 Charge/discharge curves of the $LiCoO_2 ||TiNb_2O_7$ pouch cell for the electrochemical formation.



Fig. S9 The value of median voltage difference of charge/discharge profiles for $LiCoO_2$ ||TiNb₂O₇ pouch cell at various current densities.



Fig. S10 The XRD patterns of the MSC-TiNb₂O₇ electrodes after charge/discharge cycling (a) under 40 *C* for 5 cycles and (d) 10 *C* for 50 cycles, respectively. The SEM images of the MSC-TiNb₂O₇ electrodes after charge/discharge cycling (b,c) under 40 *C* for 5 cycles and (e,f) 10 *C* for 50 cycles, respectively.

The XRD patterns of the MSC-TiNb₂O₇ electrodes after charge/discharge cycling under 40 *C* for 5 cycles and 10 *C* for 50 cycles showed sharp peaks with high intensity for Wadsley-Roth phase (PDF#70-2009), respectively, which indicated the high crystallinity of these cycled samples. Besides, the results of SEM investigation showed well maintained structure of the cycled MSC-TiNb₂O₇ at both electrode and particle levels.



Fig. S11 Full survey XPS spectrum of micrometer-scale single crystalline TiNb₂O₇.



Fig. S12 Linear relationship plots between the real impedance (Z') and reciprocal square root of angular frequency ($\omega^{-1/2}$) at the low frequency for the MSC-TiNb₂O₇ electrode before and after the initial cycle.

The linear relationships were shown between the real impedance (Z') and reciprocal square root of angular frequency ($\omega^{-1/2}$) at the low frequency for MSC-TiNb₂O₇ electrodes before and after initial charge/discharge cycle. It is worth noting the Li⁺ diffusion coefficient (D_{Li}⁺) of the MSC-TiNb₂O₇ can be estimated according to the linear relationship from the following equations:

$$\frac{R^2 T^2}{D_{Li}^{+} = 2n^4 F^4 \delta_w^2 A^4 C^4}$$

Z'=Rs+Rct+ $\delta_w w^{-1/2}$

In two formulas, the R represents the gas constant, T defines as absolute temperature, n is number of electrons per molecule during reaction, F is the Faraday's constant, A is the surface area of the work electrode, and C is the Li⁺ concentration. Furthermore, Rs and Rct represent the ohmic resistance and charge transfer resistance, respectively. The D_{Li}^+ of the MSC-TiNb₂O₇ electrodes before and after initial charge/discharge cycle could be directly estimated by the linear relationship between Z' and $\omega^{-1/2}$. In other words, D_{Li}^+ decreased with the value of the linear relationship. The reduced slope values suggested enhanced Li⁺ diffusion capability of the MSC-TiNb₂O₇ electrode after the initial cycle.



Fig. S13 The locally enlarged image of CV profiles at the sweep rate of 0.1 mV s^{-1} for the initial three cycles.



Fig. S14 The GITT curves of TNO for the (a) discharge and (b) charge processes for the initial two cycles.

3. Supplementary Tables

 Table S1. Summary of the crystal analyses by Rietveld refinements of the micrometer

 scale single crystalline TiNb₂O₇.

<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
20.37	3.80	11.89

Table S2. Table S1. Rietveld refinement results of micrometer-scale single crystalline TiNb₂O₇.

C2/m, α=γ=90°, β=120.21°			
Atom	x	У	Z
Ti1	0.00000	0.00000	0.00000
Nb1	0.00000	0.00000	0.00000
Ti2	0.18514	0.00000	0.00402
Nb2	0.18514	0.00000	0.00402
Ti3	0.07622	0.00000	0.63425
Nb3	0.07622	0.00000	0.63425
Ti4	0.89111	0.00000	0.63296
Nb4	0.89111	0.00000	0.63296
Ti5	0.29479	0.00000	0.37208
Nb5	0.29479	0.00000	0.37208
01	0.16307	0.00000	0.58804
O2	0.37909	0.00000	0.61363
O3	0.59462	0.00000	0.62068
O4	0.79361	0.00000	0.62380
O5	0.23913	0.00000	0.16612
O6	0.70382	0.00000	0.00370
O7	0.90983	0.00000	0.99507
O8	0.01078	0.00000	0.39340
09	0.86046	0.00000	0.15968
O10	0.50000	0.00000	0.00000
011	0.05115	0.00000	0.19414

Atom	Wyckoff	Occupancy
Til	2a	0.3333
Nb1	2a	0.6667
Ti2	4i	0.3333
Nb2	4i	0.6667
Ti3	4i	0.3333
Nb3	4i	0.6667
Ti4	4i	0.3333
Nb4	4i	0.6667
Ti5	4i	0.3333
Nb5	4i	0.6667

Table S3. Summary of the occupancy of the Nb and Ti ions in the micrometer-scale single crystalline TiNb₂O₇.

Table S4. The values of interplanar spacing (d) for different crystallographic plane

crystallographic planes	<i>d</i> values of measured (nm)	d values of theoretical (nm)
(40-1)	0.5059	0.5075
(21-1)	0.3432	0.3527
(61-2)	0.2483	0.2529

Table S5. The values of angle between different crystallographic plane

angles	values of measured (°)	values of theoretical (°)
(40-1) and (21-1)	70.69	70.57
(40-1) and (61-2)	42.69	42.54

Table S6. The average Li⁺ diffusion coefficient of TNO electrodes verified by GITT measurement for our work and previous literatures at discharge and charge process.

TNO	discharge	charge
This work	2.17*10 ⁻¹⁰ cm ² s ⁻¹	2.43*10 ⁻¹⁰ cm ² s ⁻¹
[7]	2.1*10 ⁻¹² cm ² s ⁻¹	2.4*10 ⁻¹² cm ² s ⁻¹
[8]	6.87*10 ⁻¹³ cm ² s ⁻¹	8.32*10 ⁻¹³ cm ² s ⁻¹
[9]	9.15*10 ⁻¹² cm ² s ⁻¹	1.22*10 ⁻¹² cm ² s ⁻¹

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