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Supporting Information

Coarse-grained Reduced $\text{Mo}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_{7+x}$ Anodes for High-Rate Lithium-ion Batteries

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Supplementary Figures S1~S14

Supplementary Tables S1~S8

Supplementary References S1~S31

Supplementary Figures

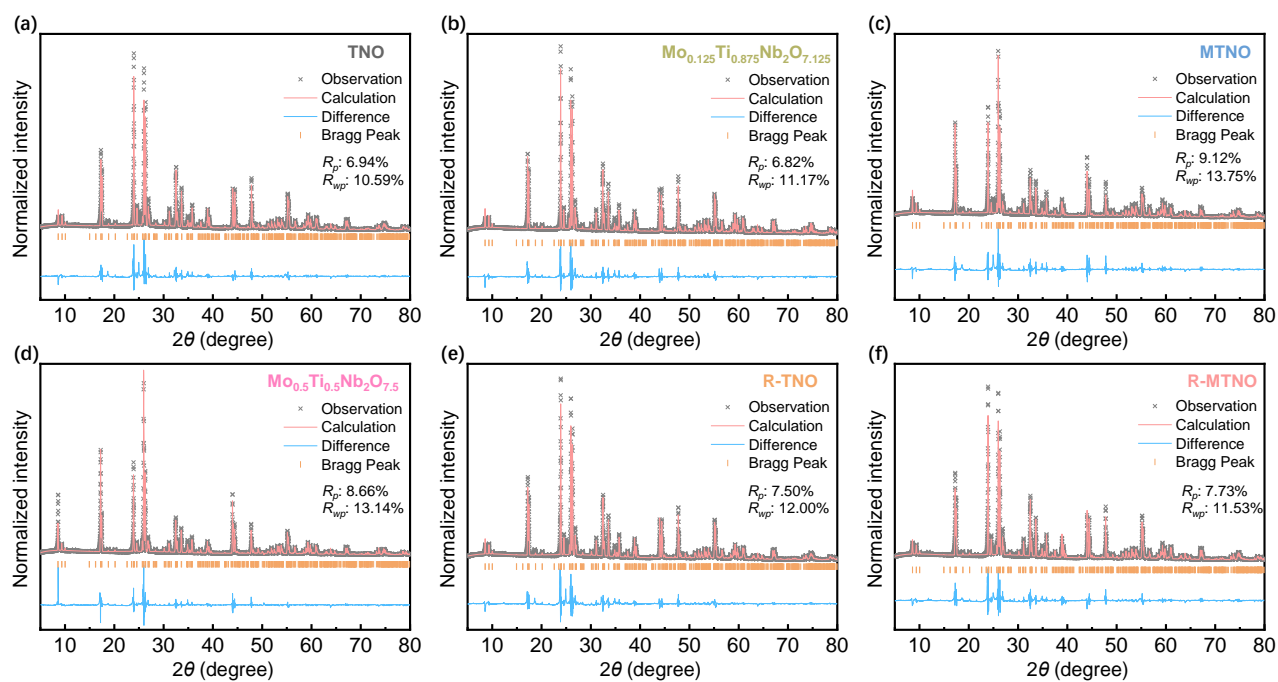


Fig. S1. XRD pattern as well as the Rietveld refinement analysis of (a) TNO, (b) $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, (c) MTNO, (d) $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$, (e) R-TNO and (f) R-MTNO. More details are shown in Table S2.

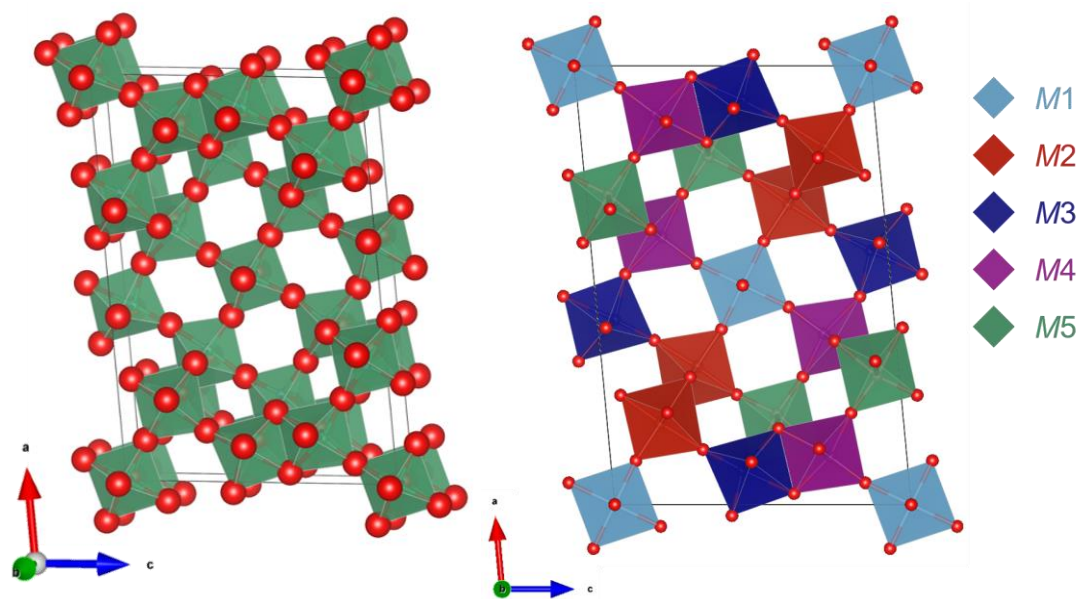


Fig. S2. Crystal structure (left) and schematic polyhedron packing (right) of TiNb_2O_7 . More details about atomic occupancy information are shown in Table S3.

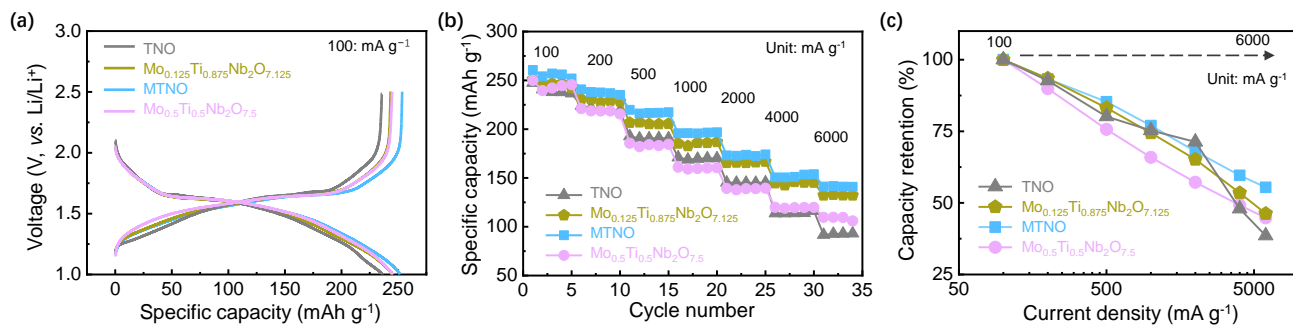


Fig. S3. (a) Galvanostatic discharge/charge profiles, (b) Rate performances, (c) rate capacity retention of TNO, $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, MTNO, and $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$.

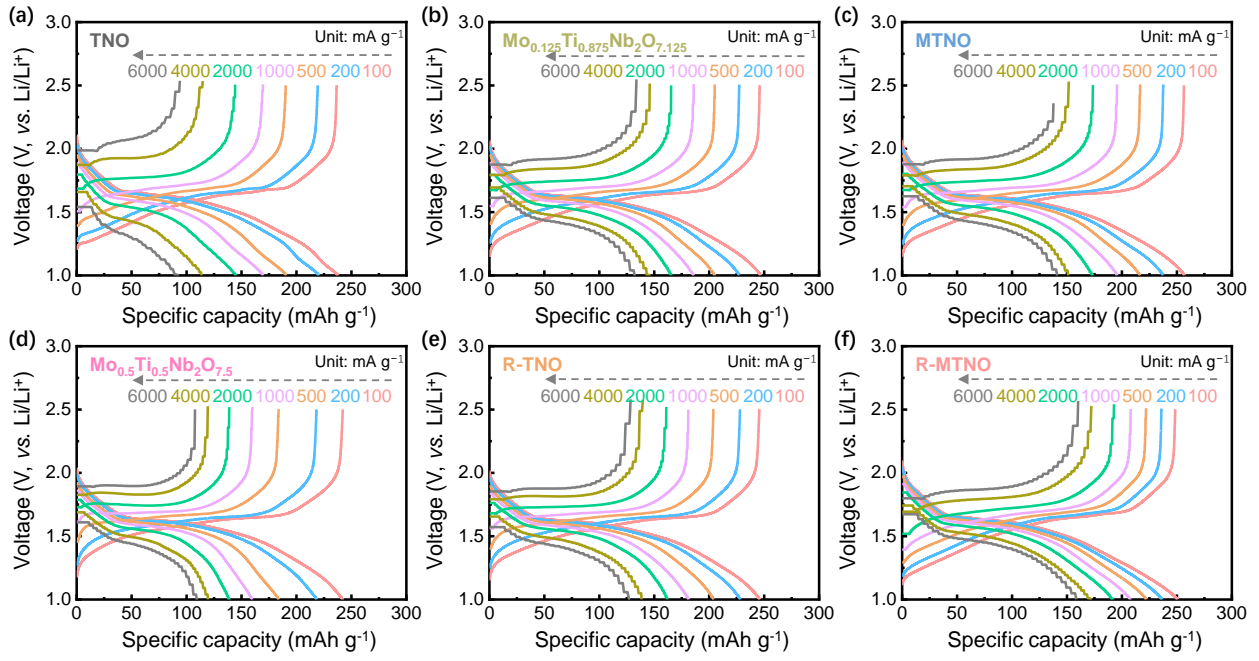


Fig. S4. Galvanostatic discharge/charge profiles at different current densities of (a) TNO, (b) $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, (c) MTNO, (d) $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$, (e) R-TNO and (f) R-MTNO.

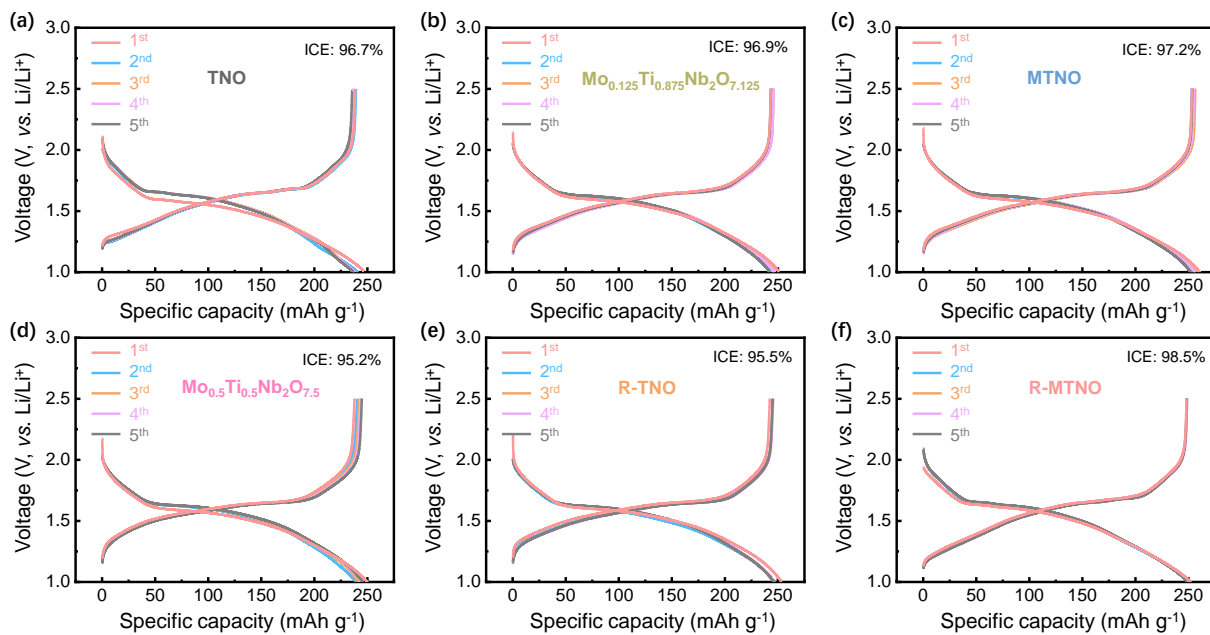


Fig. S5. Galvanostatic discharge/charge profiles at 100 mA g^{-1} for the first five cycles of (a) TNO, (b) $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, (c) MTNO, (d) $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$, (e) R-TNO and (f) R-MTNO.

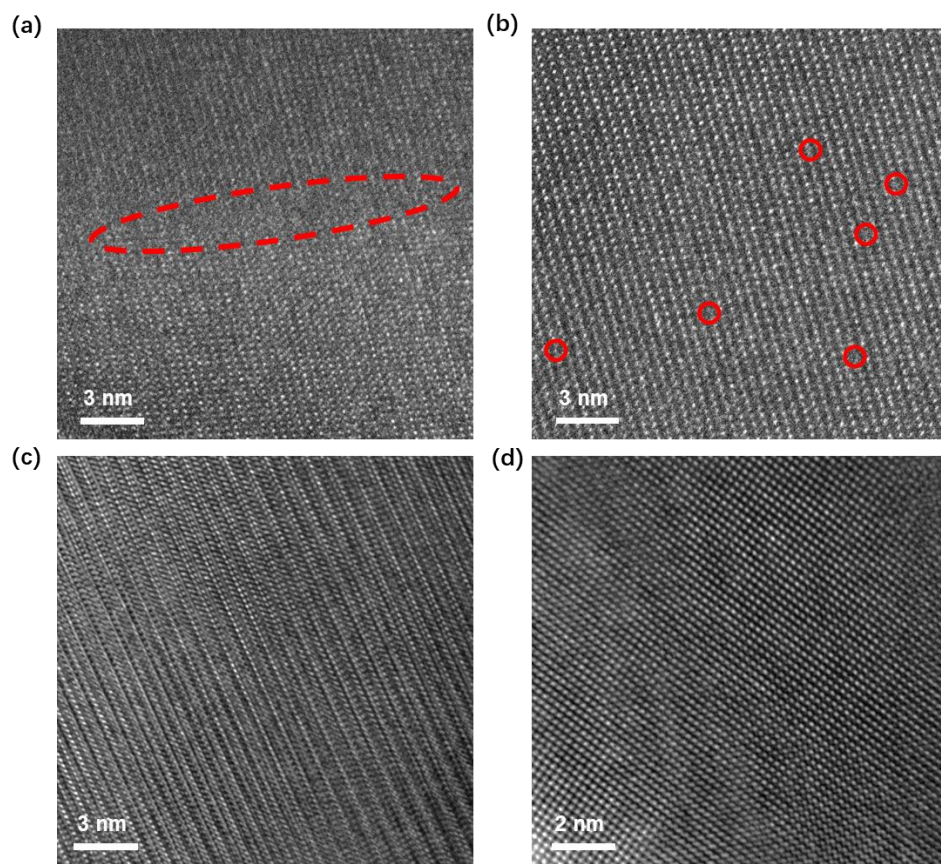


Fig. S6. HRTEM images of (a, b) R-MTNO showing more disorders and defect than (c, d) MTNO.

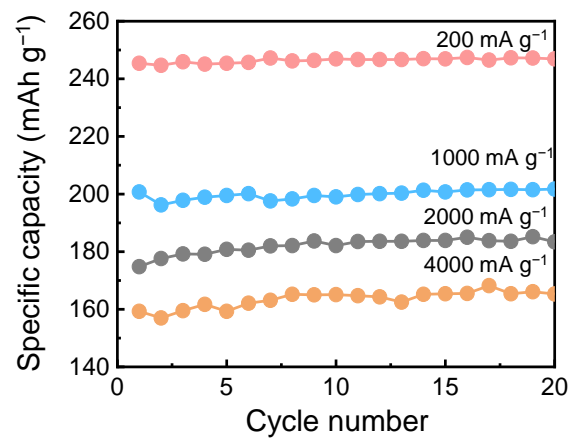


Fig. S7. Cycling performance of R-MTNO at 200, 1000, 2000 and 4000 mA g⁻¹ for the first 20 cycles.

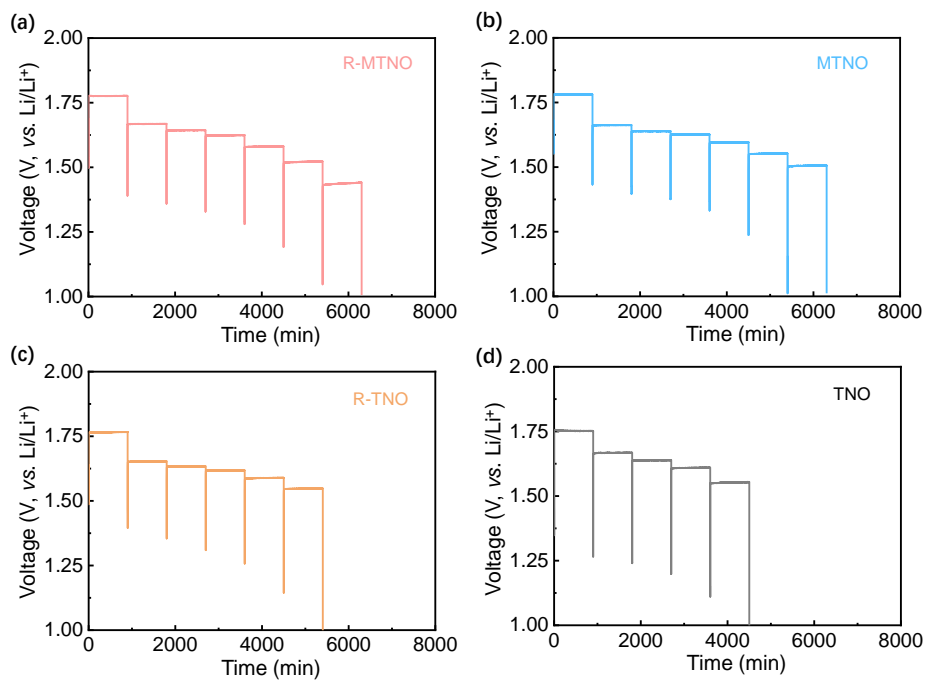


Fig. S8. GITT curves at 4000 mA g^{-1} for R-MTNO, MTNO, R-TNO and TNO electrodes.

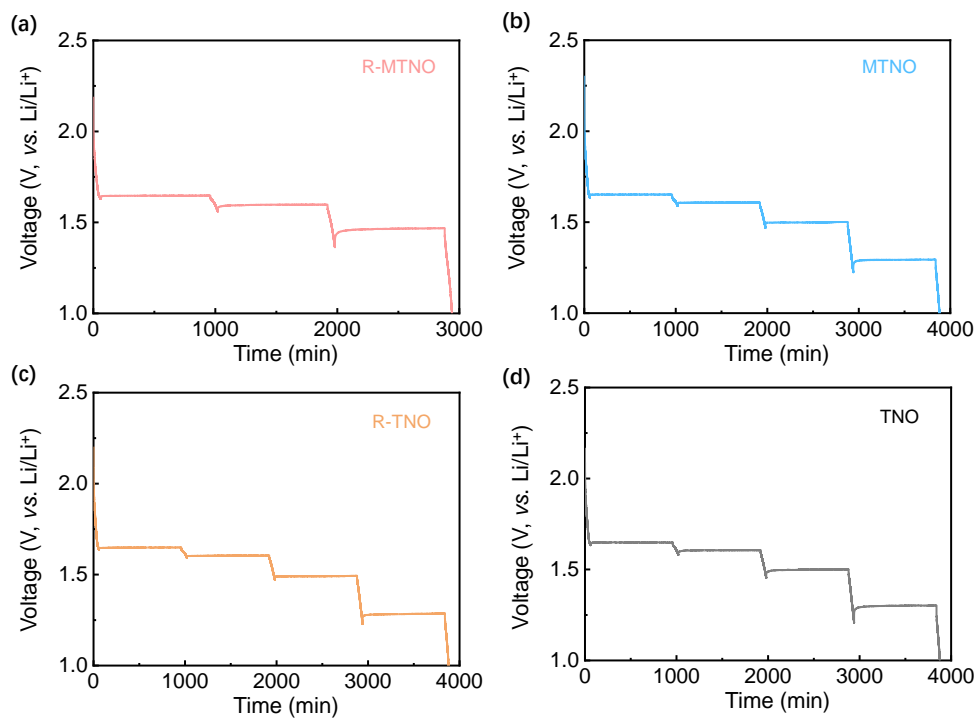


Fig. S9. GITT curves at 50 mA g⁻¹ for R-MTNO, MTNO, R-TNO and TNO electrodes.

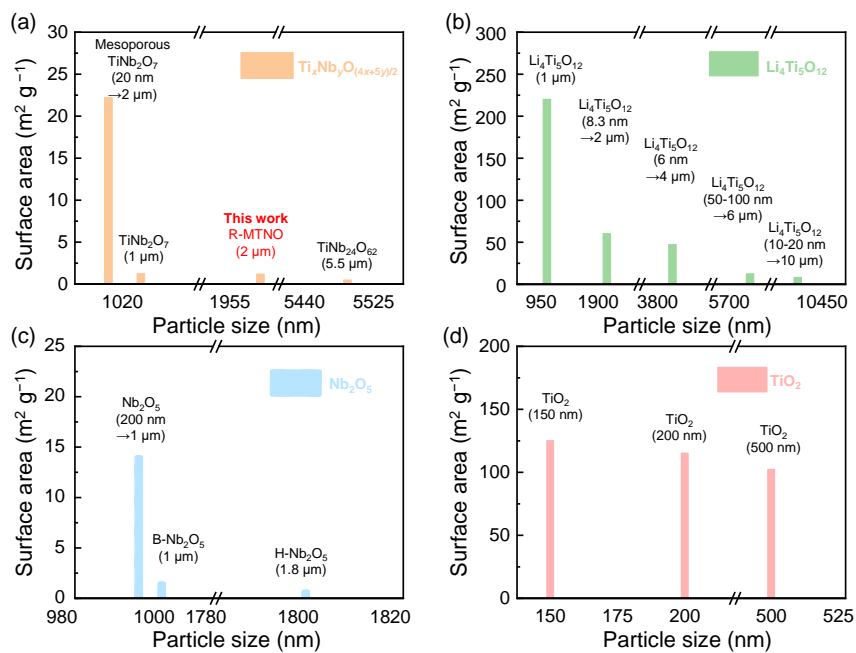


Fig. S10. Particle size versus specific surface area of representative $\text{Ti}_x\text{Nb}_y\text{O}_{(4x+5y)/2}$, Nb_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 electrodes. More details are shown in **Table S5**.

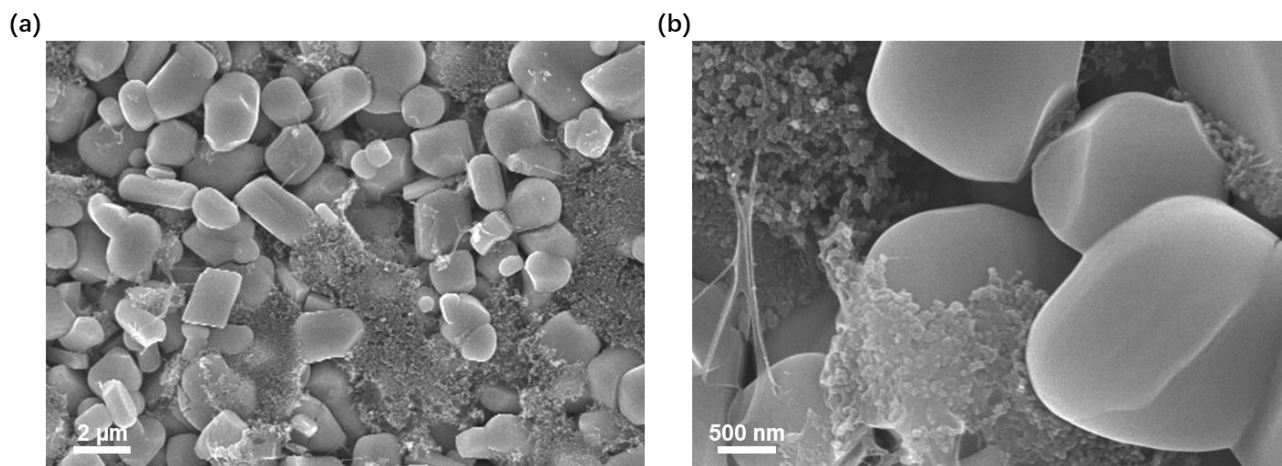


Fig. S11. SEM images for R-MTNO electrodes before cycling.

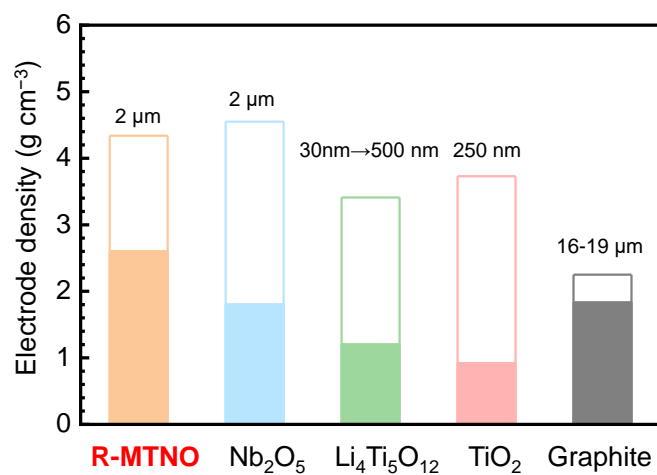


Fig. S12. Particle size and electrode density of $\text{Mo}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_{7+x}$, representative Nb_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 and graphite. Solid bar represents real density; integral hollow bar represents theoretical density. More details are shown in **Table S6**.

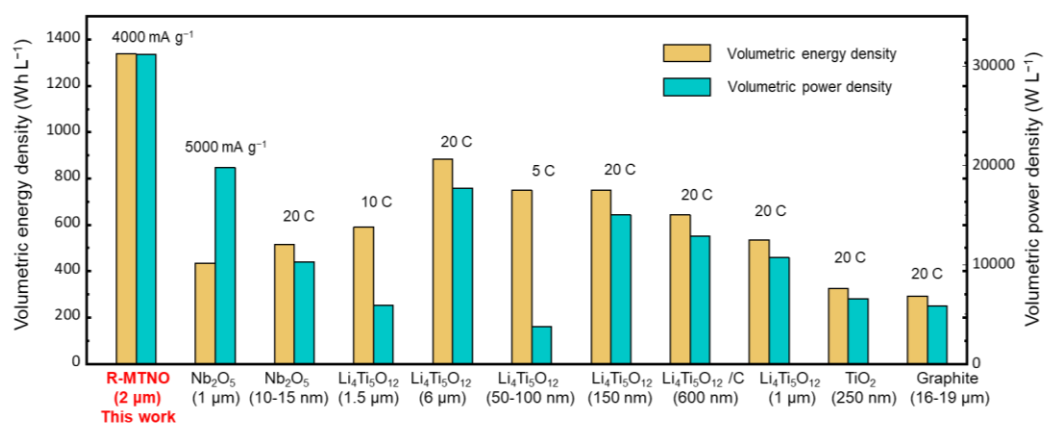


Fig. S13. Volumetric energy densities and power densities based on the anode (without current collector) of $\text{Mo}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_{7+x}$, representative Nb_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , and graphite by using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the reference cathode. More details are shown in **Table S7**.

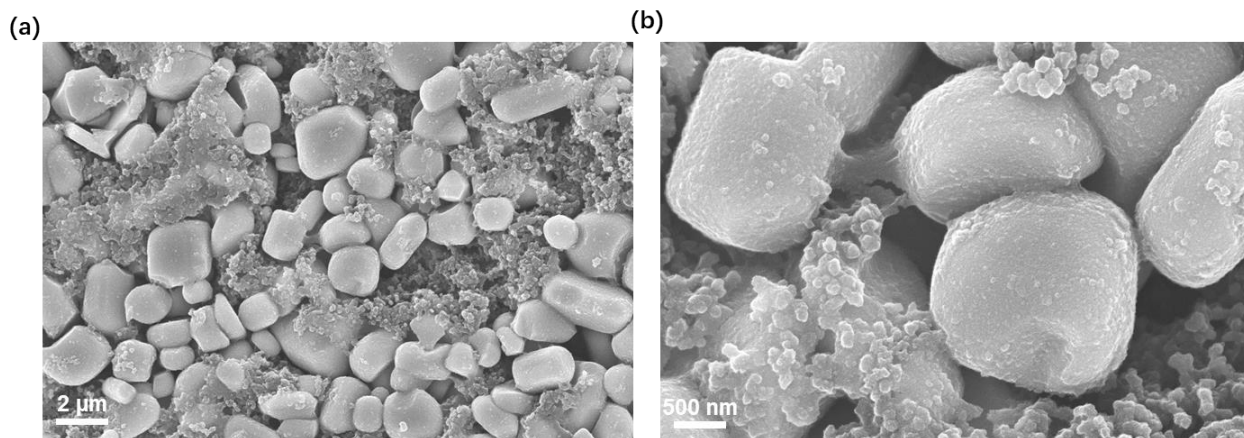


Fig. S14. SEM images for R-MTNO electrodes after 500 cycles at 2000 mA g⁻¹.

Supplementary Tables

Table S1 Compositions of TNO, $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, MTNO, $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$ measured by inductively coupled plasma atomic emission spectroscopy (ICP-MS).

Targeted composition	Measured composition
TiNb_2O_7 (TNO)	$\text{Ti}_{1.03}\text{Nb}_{1.97}\text{O}_{6.99}$
$\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$	$\text{Mo}_{0.11}\text{Ti}_{0.89}\text{Nb}_{1.99}\text{O}_{7.11}$
$\text{Mo}_{0.25}\text{Ti}_{0.75}\text{Nb}_2\text{O}_{7.25}$ (MTNO)	$\text{Mo}_{0.30}\text{Ti}_{0.73}\text{Nb}_{1.97}\text{O}_{7.29}$
$\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$	$\text{Mo}_{0.65}\text{Ti}_{0.47}\text{Nb}_{1.88}\text{O}_{7.59}$

Table S2 Rietveld refinement results TNO, $\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$, MTNO, $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$, R-TNO and R-MTNO. (Because of the structural complexity, the present powder diffraction data do not allow accurate refinements for atomic occupancies.)

Materials	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
TNO	17.68	3.80	11.90	90.00	95.32	90.00
$\text{Mo}_{0.125}\text{Ti}_{0.875}\text{Nb}_2\text{O}_{7.125}$	17.68	3.80	11.90	90.00	95.32	90.00
MTNO	17.68	3.80	11.89	90.00	95.32	90.00
$\text{Mo}_{0.5}\text{Ti}_{0.5}\text{Nb}_2\text{O}_{7.5}$	17.68	3.80	11.90	90.00	95.31	90.00
R-TNO	17.68	3.80	11.90	90.00	95.32	90.00
R-MTNO	17.67	3.80	11.89	90.00	95.33	90.00

Table S3 Atomic occupancy information of TiNb₂O₇[S1].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	Site	Polyhedron
Nb1	0.00000	0.00000	0.00000	0.909	2 <i>a</i>	<i>M1</i>
Ti1	0.00000	0.00000	0.00000	0.091	2 <i>a</i>	<i>M1</i>
Nb2	0.18528	0.00000	0.17993	0.798	4 <i>i</i>	<i>M2</i>
Ti2	0.18528	0.00000	0.17993	0.202	4 <i>i</i>	<i>M2</i>
Nb3	0.07842	0.00000	-0.55844	0.643	4 <i>i</i>	<i>M3</i>
Ti3	0.07842	0.00000	-0.55844	0.357	4 <i>i</i>	<i>M3</i>
Nb4	0.88938	0.00000	0.25857	0.727	4 <i>i</i>	<i>M4</i>
Ti4	0.88938	0.00000	0.25857	0.273	4 <i>i</i>	<i>M4</i>
Nb5	0.29286	0.00000	-0.07479	0.376	4 <i>i</i>	<i>M5</i>
Ti5	0.29286	0.00000	-0.07479	0.624	4 <i>i</i>	<i>M5</i>
O1	0.17350	0.00000	-0.42330	1.000	4 <i>i</i>	/
O2	0.37287	0.00000	-0.20690	1.000	4 <i>i</i>	/
O3	0.59702	0.00000	-0.02520	1.000	4 <i>i</i>	/
O4	0.79131	0.00000	0.17440	1.000	4 <i>i</i>	/
O5	0.24932	0.00000	0.05400	1.000	4 <i>i</i>	/
O6	0.70916	0.00000	0.70590	1.000	4 <i>i</i>	/
O7	0.89988	0.00000	-0.08510	1.000	4 <i>i</i>	/
O8	0.02523	0.00000	-0.39200	1.000	4 <i>i</i>	/
O9	0.87451	0.00000	0.68530	1.000	4 <i>i</i>	/
O10	0.50000	0.00000	0.50000	1.000	2 <i>b</i>	/
O11	0.04964	0.00000	-0.14790	1.000	4 <i>i</i>	/

Table S4 Specific surface area and first-cycle Coulombic efficiency of R-MTNO, MTNO, R-TNO and TNO.

Materials	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	First-cycle Coulombic efficiency (%)
R-MTNO	1.1	98.5
MTNO	1.5	97.2
R-TNO	1.5	95.5
TNO	1.0	96.7

Table S5 Particle size versus specific surface area of representative $Ti_xNb_yO_{(4x+5y)/2}$, Nb_2O_5 , $Li_4Ti_5O_{12}$ and TiO_2 electrodes.

Materials	Particle size (μm)	Specific surface area ($m^2 g^{-1}$)	Refs
R-MTNO	2.0	1.2	This work
Porous $TiNb_{24}O_{62}$	5.5	0.5	[S2]
$TiNb_2O_7$	1.5	1.3	[S3]
Mesoporous $TiNb_2O_7$	1.0	22.2	[S3]
H- Nb_2O_5	1.8	0.7	[S4]
B- Nb_2O_5	1.2	1.5	[S4]
Nb_2O_5 microsphere	1.0	14.0	[S5]
TiO_2	0.5	102.1	[S6]
TiO_2	0.2	115.0	[S7]
TiO_2	0.2	125.0	[S8]
Carbon-coated $Li_4Ti_5O_{12}$	10.0	8.1	[S9]
$Li_4Ti_5O_{12}$	6.0	12.1	[S10]
Porous $Li_4Ti_5O_{12}$	4.0	51.3	[S11]
Mesoporous $Li_4Ti_5O_{12}$	2.0	60.2	[S12]
$Li_4Ti_5O_{12}$ microspheres	1.0	220.0	[S13]

Table S6 Particle size and electrode density of $\text{Mo}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_{7+x}$, representative Nb_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 and graphite.

Materials	Particle size (μm)	Electrode density (g cm^{-3})	Refs
R-MTNO	2.0	2.6	This work
Nb_2O_5	2.0	1.8 ^a	[S4]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	0.8~3.0	2.0	[S14]
TiO_2	0.3 ^b	0.9	[S15]
Graphite	16~19	1.8	[S16]

a: Tap density of the material.

b: The average length and diameter are 2 μm and 0.3 μm , respectively.

Table S7 Electrochemical comparison table considering the particle size, specific surface area, electrode densities, initial CE, volumetric energy density and volumetric power density among $\text{Mo}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_{7+x}$ and representative Nb_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 and graphite. The electrode compositions (mass ratio of active materials: conductive carbon: binder (binder)) are listed for references.

Materials	Surface area ($\text{m}^2 \text{g}^{-1}$)	Electrode composition	Electrode density (g cm^{-3})	Initial CE (%)	High-rate capacity (mAh g^{-1})	Volumetric energy density [Wh L^{-1}]	Volumetric power density [W L^{-1}]	Refs
R-MTNO	1.1	90:5:2.5:2.5	2.6	99	192 (2000 mA g^{-1})	1338	31200	This work
MTNO	1.5	90:5:2.5:2.5	2.6	97	173 (2000 mA g^{-1})	1179	31200	This work
R-TNO	1.5	90:5:2.5:2.5	2.6	96	161 (2000 mA g^{-1})	1080	31200	This work
TNO	1.0	90:5:2.5:2.5	2.6	97	145 (2000 mA g^{-1})	888	31200	This work
Nb_2O_5 (150 nm→1 μm)	22.4	80:10:10	$\approx 1.5^a$	92 ^b	140 (2000 mA g^{-1})	436	19800	[S5]
Nb_2O_5 (10~15 nm pressed)	83.0	85:15	1.5	90 ^b	130 (20 C)	515	10296	[S17]
Carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (10~20 nm→1.5 μm)	3.1	80:10:10	1.3 ^c	97 ^b	110 (10 C)	590	5896	[S18]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (50~100 nm→6 μm)	12.1	80:10:10	1.2 ^c	96 ^b	165 (20 C)	884	17688	[S10]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoclusters (50~100 nm)	142.0	80:10:10	0.8 ^c	97 ^b	140 (5 C)	750	3752	[S19]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (150 nm)	46.4	80:10:10	1.2 ^c	N/A	140 (20 C)	750	15008	[S20]
$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ (30 nm→600 nm)	8.6	80:10:10	1.2 ^c	N/A	120 (20 C)	643	12864	[S21]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres (1 μm)	20.0	80:10:10	$\approx 1.2^{a,c}$	84 ^b	100 (20 C)	536	10720	[S22]
TiO_2 (250 nm)	N/A	80:10:10	0.92	84 ^b	200 (0.17 C) 130 (20 C)	327	6530	[S15, 23]
Graphite (16~19 μm)	2.0	92:3:5	1.83	94	36 (20 C)	293	5857	[S16, 24]

a: Estimated by specific surface area.

b: Calculated from the initial voltage capacity curve.

c: Tap density of the material. The calculation of volumetric energy density and power density was based on the electrode density of commercialized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (2.0 g cm^{-3}).

d: The volumetric energy density and volumetric power density were calculated by the following equations (for the average voltage, we assume charge voltage of 4.9 V for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode):

$$\text{Volumetric energy density (Wh L}^{-1}\text{)} = \frac{(\text{Cell capacity}) \times (\text{Average voltage})}{(\text{Electrode area}) \times (\text{Thickness of anode including active materials, binder and carbon black})}$$

$$\text{Volumetric power density (W L}^{-1}\text{)} = \frac{(\text{Cell capacity}) \times (\text{Average voltage})}{(\text{Discharging time of anode}) \times (\text{Electrode area}) \times (\text{Thickness of anode including active materials, binder and carbon black})}$$

Table S8 Electrochemical comparison table considering the mass loading, particle size, rate capability and cyclability among recent reported $\text{Ti}_x\text{Nb}_y\text{O}_{(4x+5y)/2}$ electrodes.

Materials	Mass loading (mg cm^{-2})	Particle size	Rate capability (mAh g^{-1})	Cyclability (mAh g^{-1})	Refs
R-MTNO	1~2	2 μm	158 (6000 mA g^{-1})	500 cycles (2000 mA g^{-1}, 75%)	This work
MTNO	1~2	2 μm	141 (6000 mA g^{-1})	500 cycles (2000 mA g^{-1}, 58%)	This work
R-TNO	1~2	2 μm	126 (6000 mA g^{-1})	500 cycles (2000 mA g^{-1}, 65%)	This work
TNO	1~2	2 μm	92 (6000 mA g^{-1})	500 cycles (2000 mA g^{-1}, 29%)	This work
TiNb_2O_7	1~1.2	100 nm	150 (20 C)	50 cycles (1 C, 90%)	[S25]
$\text{Ti}_2\text{N}_{10}\text{O}_{29-x}\text{@C}$	2	50 nm	200 (20 C)	500 cycles (10 C, 98.7%)	[S26]
$\text{TiNb}_2\text{O}_7/\text{C}$	1.6~1.8	800 nm	194 (10 C)	500 cycles (5 C, 47%)	[S27]
TiNb_2O_7	N/A	100 nm→3 μm	125 (10 C)	500 cycles (10 C, 73%)	[S28]
$\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$	N/A	2 μm	120 (20 C)	800 cycles (10 C, 85%)	[S29]
TiNb_2O_7	N/A	100 nm	230 (20 C)	1000 cycles (10 C, 81%)	[S30]
TiNb_2O_7	1.5	1 μm	128 (20 C)	500 cycles (10 C, 32%)	[S3]
$\text{TiNb}_{24}\text{O}_{62}$	N/A	50 nm→2 μm	181 (20 C)	500 cycles (10 C, 90.5%)	[S2]
TiNb_2O_7	1.5	50 nm	150 (10 C)	1000 cycles (10 C, 75%)	[S31]

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