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Supporting Information

MoNb₁₂O₃₃ as a new anode material for high-capacity, safe, rapid and durable Li⁺ storage: structural characteristics, electrochemical properties and working mechanisms

Xiangzhen Zhu^{a,b}, Jian Xu^b, Yunpeng Luo^b, Qingfeng Fu^b, Guisheng Liang^b, Lijie

Luo^b, Yongjun Chen^b, Chunfu Lin^{*a,b}, X. S. Zhao^{*a,c}

^a Institute of Materials for Energy and Environment, School of Materials Science and

Engineering, Qingdao University, Qingdao 266071, China

^b State Key Laboratory of Marine Resource Utilization in South China Sea, School of

Materials Science and Engineering, Hainan University, Haikou 570228, China

^c School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane,

QLD 4072, Australia

*Corresponding authors. E-mail addresses: linchunfu@qdu.edu.cn (C. Lin);

george.zhao@uq.edu.au (X. Zhao).

Detailed process of Rietveld refinement

Since this is the first fabrication of MoNb₁₂O₃₃, no existing crystal data for MoNb₁₂O₃₃ can be found in previous reports. However, on the basis of the known crystal data of WNb₁₂O₃₃, the detailed crystal structure of MoNb₁₂O₃₃ was successfully clarified through a Rietveld refinement. First, the "cif" (Crystallographic Information File) file of WNb₁₂O₃₃ was imported into the GSAS program. Second, in the program, "W" was changed to "Mo". Third, two files respectively containing the instrumental parameters and experimental diffraction data were imported into the program. Finally, the following instrumental and structural parameters were successively refined: background parameters, zero-shift, unit-cell parameters, profile parameters, atomic fractional coordinates, and atomic isotropic displacement parameters. All isotropic temperature factors were fixed to be the same. The site occupancies were assumed to fulfill the stoichiometric composition of MoNb₁₂O₃₃.



Fig. S1. XRD patterns of P-MoNb $_{12}O_{33}$ calcined at 650, 660, 670 and 680 °C.



Fig. S2. (a, b) FESEM, (c) TEM and (d) EDX mapping images of M-MoNb₁₂O₃₃.



Fig. S3. (a) HRTEM image and (b) SAED pattern of M-MoNb₁₂O₃₃.



Fig. S4. Nyquist plots of M-MoNb₁₂O₃₃ and P-MoNb₁₂O₃₃ (*inset*: selected equivalent circuit).

As can be seen in Fig. S4, each Nyquist plot consists of two depressed semicircles and one slope. According to a previous study [S1], the semicircle observed in the high-frequency region refers to the synergistic effect of the Li⁺ desolvation, electron transfer and adsorption, which is denoted as the R_1 /CPE₁ pair in the equivalent circuit (Fig. S4 *inset*). The other semicircle observed in the medium-

frequency region is associated with the Li⁺ insertion at the MoNb₁₂O₃₃ particle surfaces (the R_2 /CPE₂ pair). The slope observed in the low-frequency region corresponds to the Warburg resistance (W), representing the Li⁺ diffusion in the MoNb₁₂O₃₃ lattice. R_b in the equivalent circuit embodies the Ohmic resistance of the cell, primarily originating from the electrolyte. The fitted R_1 and R_2 values for the M-MoNb₁₂O₃₃ sample are 248 and 1047 Ω , respectively. In contrast, those for the P-MoNb₁₂O₃₃ sample were significantly decreased to 109 and 293 Ω . Therefore, the porous microspheres with small primary particles enabled faster Li⁺ desolvation, electron transfer, adsorption and Li⁺ insertion at the active particle surfaces, further confirming the better electrochemical kinetics of P-MoNb₁₂O₃₃. This finding coincides with the CV (Fig. 4a) and galvanostatic discharge–charge (Fig. 4b) results.



Fig. S5. (a, b) *Ex*-FESEM images of P-MoNb₁₂O₃₃ electrode at 10C after 1000 cycles.



Fig. S6. (a) CV curves of M-MoNb₁₂O₃₃ from 0.2 to 1.1 mV s⁻¹. (b) Calculation of *a*-values for M-MoNb₁₂O₃₃ by using relationship between peak current and sweep rate.
(c) Pseudocapacitive contribution ratio of M-MoNb₁₂O₃₃ at different sweep rates. (d) Pseudocapacitive contribution of M-MoNb₁₂O₃₃ at 1.1 mV s⁻¹.



Fig. S7. Relationship between peak current of cathodic/anodic reaction (I_p) and square root of sweep rate ($v^{0.5}$) for M-MoNb₁₂O₃₃.



Fig. S8. XRD pattern of LiMn₂O₄ in this work.



Fig. S9. (a, b) FESEM images of LiMn₂O₄ in this work.



Fig. S10. Charge–discharge profiles of LiMn₂O₄ in this work at 0.1C.

atom	site	x	у	Z
Мо	2a	0	0.25	0
Nb1	4 <i>c</i>	0.367537	0	0.044215
Nb2	4 <i>c</i>	0.246574	0	0.135585
Nb3	4 <i>c</i>	0.130339	0	0.230816
Nb4	4 <i>c</i>	0.416347	0	0.377805
Nb5	4 <i>c</i>	0.295871	0	0.474168
Nb6	4 <i>c</i>	0.467645	0	0.715923
01	2b	0	0.5	0.5
02	4 <i>c</i>	0.161909	0	-0.007014
O3	4 <i>c</i>	0.296566	0	0.089035
O4	4 <i>c</i>	0.020596	0	0.083760
O5	4 <i>c</i>	0.452604	0	0.157945
O6	4 <i>c</i>	0.187949	0	0.176336
O7	4 <i>c</i>	0.053749	0	0.267702
08	4 <i>c</i>	0.311234	0	0.236494
09	4 <i>c</i>	0.479191	0	0.323294
O10	4 <i>c</i>	0.217692	0	0.356493
O11	4 <i>c</i>	0.347232	0	0.425273
012	4 <i>c</i>	0.224570	0	0.528960
O13	4 <i>c</i>	0.383602	0	0.603455
O14	4 <i>c</i>	0.079680	0	0.626197
015	4 <i>c</i>	0.381981	0	0.755691
O16	4 <i>c</i>	0.271839	0	0.893514
O17	4 <i>c</i>	0.426748	0	0.976852

Table S1. Fractional atomic parameters of $MoNb_{12}O_{33}$ with C2 space group.

sample	potential at	potential at	potential	
Sumpre	cathodic peak (V)	anodic peak (V)	difference (V)	
M-MoNb ₁₂ O ₃₃				
(Mo ⁴⁺ /Mo ⁵⁺ ,				
Mo^{5+}/Mo^{6+} and	1.723	1.837	0.114	
Nb ⁴⁺ /Nb ⁵⁺)				
P-MoNb ₁₂ O ₃₃				
(Mo ⁴⁺ /Mo ⁵⁺ ,				
Mo^{5+}/Mo^{6+} and	1.787	1.843	0.056	
Nb4+/Nb5+)				
M-MoNb ₁₂ O ₃₃				
(Nb ³⁺ /Nb ⁴⁺)	1.113	1.434	0.321	
P-MoNb ₁₂ O ₃₃	1.102			
(Nb^{3+}/Nb^{4+})	1.183	1.321	0.138	

Table S2. Potentials at cathodic/anodic CV peaks and potential differences of M- $MoNb_{12}O_{33}/Li$ and P-MoNb₁₂O₃₃/Li cells at 0.2 mV s⁻¹ (2nd cycle).

material	theoretical capacity	practical capacity	reference
material	$(mAh g^{-1})$	$(mAh g^{-1})$	
P-MoNb ₁₂ O ₃₃	401	321	this work
M-MoNb ₁₂ O ₃₃	401	294	this work
graphite	372	310	[S2]
$Li_4Ti_5O_{12}$	175	169	[S3]
$TiNb_2O_7$	388	281	[S4]
$Ti_2Nb_{10}O_{29}$	396	247	[S5]
TiNb ₂₄ O ₆₂	402	296	[S6]
TiNb ₆ O ₁₇	397	328	[S7]
Nb ₂ O ₅	403	210	[S8]
Nb ₁₂ O ₂₉	374	287	[S9]
Nb ₂₅ O ₆₂	396	289	[S9]
FeNb ₁₁ O ₂₉	400	270	[S10]
GaNb ₁₁ O ₂₉	379	264	[S11]
$ZrNb_{24}O_{62}$	388	320	[S12]
$Cr_{0.5}Nb_{24.5}O_{62}$	403	344	[S13]
GeNb ₁₈ O ₄₇	386	217	[S14]
PNb ₉ O ₂₅	381	200	[S15]
VNb ₉ O ₂₅	416	220	[S16]
$W_9Nb_8O_{47}$	289	238	[S17]

Table S3. Comparisons of practical/theoretical capacity of $M-MoNb_{12}O_{33}/P-MoNb_{12}O_{33}$ with intercalating anode materials previously reported.

material	current	electrochemical property	reference	
	rate (C)	$(mAh g^{-1})$	rererence	
P-MoNb ₁₂ O ₃₃	10	~ 208 at 1000 th cycles	this work	
M-MoNb ₁₂ O ₃₃	10	~123 at 1000 th cycles	this work	
TiNb ₂ O ₇ nanoparticles	10	~123 at 500 th cycles	[S18]	
porous TiNb ₂ O ₇ nanospheres	5	\sim 212 at 1000 th cycles	[S19]	
ordered mesostructured TiNb ₂ O ₇	10	~ 200 at 2000 th cycles	[S20]	
TiNb ₂ O ₇ nanofibers	5	\sim 133 at 100 th cycles	[S21]	
TiNb ₂ O ₇ nanorods	10	~ 140 at 100^{th} cycles	[S22]	
three-dimentional ordered macroporous TiNb ₂ O ₇	10	~ 87 at 100 th cycles	[\$23]	
$Cu_{0.02}Ti_{0.94}Nb_{2.04}O_7$	10	~ 180 at 1000^{th} cycles	[S24]	
$Ru_{0.01}Ti_{0.99}Nb_2O_7$	5	~162 at 100 th cycles	[S25]	
Ti ₂ Nb ₁₀ O ₂₉ /reduced graphene oxide	4	~ 120 at 50^{th} cycles	[S26]	
$Ti_2Nb_{10}O_{27.1}$	5	~ 164 at 100 th cycles	[S27]	
$Ti_2Nb_{10}O_{29}/Ag$	10	~ 142 at 500 th cycles	[S28]	
Ti ₂ Nb ₁₀ O ₂₉ hollow nanofibers	10	~ 123 at 500 th cycles	[829]	
porous Ti ₂ Nb ₁₀ O ₂₉ nanospheres	10	~ 141 at 1000 th cycles	[\$30]	
porous TiNb ₂₄ O ₆₂ nanospheres	10	~183 at 500 th cycles	[S6]	
TiNb ₆ O ₁₇	5	~ 171 at 100^{th} cycles	[S7]	
FeNb ₁₁ O _{27.9}	10	~ 135 at 200 th cycles	[S31]	
GeNb ₁₈ O ₄₇ nanofibers	2	~162 at 200 th cycles	[S14]	
VNb ₉ O ₂₅ nanoribbons	3	~132 at 500 th cycles	[S16]	
W9Nb8O47 nanofibers	5	~113 at 1000 th cycles	[S17]	
GaNb11O29 nanowebs	10	~153 at 1000 th cycles	[S12]	

Table S4. Comparisons of electrochemical properties of M-MoNb₁₂O₃₃ and P-MoNb₁₂O₃₃ with niobium-based oxide anode materials previously reported.

sample	Li ⁺ diffusion coefficient	Li ⁺ diffusion coefficient	nofonon o o
Jumpie	for Li ⁺ insertion (cm ² s ⁻¹)	for Li^+ extraction (cm ² s ⁻¹)	reference
MoNb ₁₂ O ₃₃	4.0×10 ⁻¹⁴	8.6×10 ⁻¹⁴	this work
TiNb ₂ O ₇	8.0×10 ⁻¹⁶	9.5×10 ⁻¹⁶	[S32]
$Ti_2Nb_{10}O_{29}$	5.4×10 ⁻¹⁵	6.5×10 ⁻¹⁵	[S27]
TiNb ₆ O ₁₇	4.3×10 ⁻¹⁴	5.5×10 ⁻¹⁴	[S7]

Table S5. Comparisons of Li^+ diffusion coefficients of $MoNb_{12}O_{33}$ with other intercalating hosts tested by the same CV method.

References

[S1]M. Nakayama, H. Ikuta, Y. Uchimoto, M. Wakihara, Study on the AC impedance spectroscopy for the Li insertion reaction of $Li_xLa_{1/3}NbO_3$ at the electrode-electrolyte interface, J. Phys. Chem. B 107 (2003) 10603–10607.

[S2]Y.P. Wu, E. Rahm, R. Holze, Carbon anode materials for lithium ion batteries, J.Power Sources 114 (2003) 228–236.

[S3]T.F. Yi, L.J. Jiang, J. Shu, C.B. Yue, R.S. Zhu, H.B. Qiao, Recent development and application of $Li_4Ti_5O_{12}$ as anode material of lithium ion battery, J. Phys. Chem. Solids 71 (2010) 1236–1242.

[S4]J.T. Han, Y.H. Huang, J.B. Goodenough, New anode framework for rechargeable lithium batteries, Chem. Mater. 23 (2011) 2027–2029.

[S5]X.Y. Wu, J. Miao, W.Z. Han, Y.S. Hu, D.F. Chen, J.S. Lee, J. Kim, L.Q. Chen, Investigation on Ti₂Nb₁₀O₂₉ anode material for lithium-ion batteries, Electrochem. Commun. 25 (2012) 39–42.

[S6]C. Yang, S.J. Deng, C.F. Lin, S.W. Lin, Y.J. Chen, J.B. Li, H. Wu, Porous $TiNb_{24}O_{62}$ microspheres as high-performance anode materials for lithium-ion batteries of electric vehicles, Nanoscale 8 (2016) 18792–18799.

[S7]C.F. Lin, G.Z. Wang, S.W. Lin, J.B. Li, L. Lu, TiNb₆O₁₇: a new electrode material for lithium-ion batteries, Chem. Commun. 51 (2015) 8970–8973.

[S8]S.F. Lou, X.Q. Cheng, L. Wang, J.L. Gao, Q. Li, Y. L. Ma, Y. Z. Gao, P.J. Zuo, C.Y. Du, G.P. Yin, High-rate capability of three-dimensionally ordered macroporous T-Nb₂O₅ through Li⁺ intercalation pseudocapacitance, J. Power Sources 361 (2017) 80–86.

[S9]R.J. Li, Y. Qin, X. Liu, L. Yang, C.F. Lin, R. Xia, S.W. Lin, Y.J. Chen, J.B. Li, Conductive $Nb_{25}O_{62}$ and $Nb_{12}O_{29}$ anode materials for use in high-performance lithium-ion storage, Electrochim. Acta 266 (2018) 202–211.

[S10]X.M. Lou, Z.H. Xu, Z.B. Luo, C.F. Lin, C. Yang, H. Zhao, P. Zheng, J.B. Li, N. Wang, Y.J. Chen, H. Wu, Exploration of Cr_{0.2}Fe_{0.8}Nb₁₁O₂₉ as an advanced anode material for lithium-ion batteries of electric vehicles, Electrochim. Acta 245 (2017) 482–488.

[S11]X.M. Lou, Q.F. Fu, J. Xu, X. Liu, C.F. Lin, J.X. Han, Y.P. Luo, Y.J. Chen, X.Y. Fan, J.B. Li, GaNb₁₁O₂₉ nanowebs as high-performance anode materials for lithiumion batteries, ACS Appl. Nano Mater. 1 (2018) 183–190. [S12]C. Yang, Y.L. Zhang, F. Lv, C.F. Lin, Y. Liu, K. Wang, J.R. Feng, X.B. Wang, Y.J. Chen, J.B. Li, S.J. Guo, Porous ZrNb₂₄O₆₂ nanowires with pseudocapacitive behavior achieve high-performance lithium-ion storage, J. Mater. Chem. A 5 (2017) 22297–22304.

[S13]C. Yang, S. Yu, C.F. Lin, F. Lv, S.Q. Wu, Y. Yang, W. Wang, Z.Z. Zhu, J.B. Li,
N. Wang, S.J. Guo, Cr_{0.5}Nb_{24.5}O₆₂ nanowires with high electronic conductivity for
high-rate and long-life lithium-ion storage, ACS Nano 11 (2017) 4217–4224.

[S14]F.M. Ran, X. Cheng, H.X. Yu, R.T. Zheng, T.T. Liu, X.F. Li, N. Ren, M. Shui, J. Shu, Nano-structured GeNb₁₈O₄₇ as novel anode host with superior lithium storage performance, Electrochim. Acta 282 (2017) 634–641.

[S15]S. Patoux, M. Dolle, G. Rousse, C. Masquelier, A reversible lithium intercalation process in an ReO₃-type structure PbNb₉O₂₅, J. Electrochem. Soc. 149 (2002) A391–A400.

[S16]S.S. Qian, H.X. Yu, L. Yan, H.J. Zhu, X. Cheng, Y. Xie, N.B. Long, M. Shui, J. Shu, High-rate long-life pored nanoribbon VNb₉O₂₅ built by interconnected ultrafine nanoparticles as anode for lithium-ion batteries, ACS Appl Mater. Interfaces 9 (2017) 30608–30616.

[S17]L. Yan, X. Cheng, H.X. Yu, H.J. Zhu, T.T. Liu, R.T. Zheng, R.F. Zhang, M. Shui, J. Shu, Ultrathin W₉Nb₈O₄₇ nanofibers modified with thermal NH₃ for superior electrochemical energy storage, Energy Storage Mater. 14 (2018) 159–168.

[S18]S.F.Lou, Y.L. Ma, X.Q. Cheng, J.L. Gao, Y.Z. Gao, P.J. Zuo, C.Y. Du, G.P. Yin, Facile synthesis of nanostructured TiNb₂O₇ anode materials with superior performance for high-rate lithium ion batteries, Chem. Commun. 51 (2015) 17293– 17296.

[S19]Q.S. Cheng, J.W. Liang, N. Lin, C. Guo, Y.C. Zhu, Y.T. Qian, Porous TiNb₂O₇ nanospheres as ultra long-life and high-power anodes for lithium-ion batteries, Electrochim. Acta 176 (2015) 456–462.

[S20]C.S. Jo, Y.S. Kim, J.K. Hwang, J.M. Shim, J.Y. Chun, J.W. Lee, Block copolymer directed ordered mesostructured TiNb₂O₇ multimetallic oxide constructed of nanocrystals as high power Li-ion battery anodes, Chem. Mater. 26 (2014) 3508–3514.

[S21]X.F. Wang, G.Z. Shen, Inercalation pseudo-capacitive TiNb₂O₇@carbon electrode for high-performance lithium ion hybrid electrochemical supercapacitors with ultrahigh energy density, Nano Energy 15 (2015) 104–114.

[S22]L. Hu, C.F. Lin, C.H. Wang, C. Yang, J.B. Li, Y.J. Chen, S.W. Lin, TiNb₂O₇ nanorods as a novel anode materials for secondary lithium-ion batteries. Funct. Mater. Lett. 9 (2016) 1642004.

[S23]S.F. Lou, X.Q. Cheng, Y. Zhao, A. Lushington, J.L. Gao, Q. Li, P.J. Zuo, B.Q. Wang, Y.Z. Gao, Y.L. Ma, C.Y. Du, G.P. Yin, X.L. Sun, Superior performance of ordered macroporous TiNb₂O₇ anodes for lithium ion batteries: understanding from the structural and pseudocapacitive insights on achieving high rate capability, Nano Energy 34 (2017) 15–25.

[S24]C. Yang, C.F. Lin, S.W. Lin, Y.J. Chen, J.B. Li, Cu_{0.02}Ti_{0.94}Nb_{2.04}O₇: an advanced anode material for lithium-ion batteries of electric vehicles, J. Power Sources 328 (2016) 336–344.

[S25]C.F. Lin, S. Yu, S.Q. Wu, S.W. Lin, Z.Z. Zhu, J.B. Li, L. Lu, Ru_{0.01}Ti_{0.99}Nb₂O₇ as an intercalation-type anode material with a large capacity and high rate performance for lithium-ion batteries, J. Mater. Chem. A 3 (2015) 8627–8635.

[S26]W.L. Wang, B. Oh, J. Park, H. Ki, J. Jang, G. Lee, H. Hu, M. Ham, Solid-state synthesis of Ti₂Nb₁₀O₂₉/reduced graphene oxide composites with enhanced lithium storage capability, J. Power Sources 300 (2015) 272–278.

[S27]C.F. Lin, S. Yu, H. Zhao, S.Q. Wu, G.Z. Wang, L. Yu, Y.F. Li, Z.Z. Zhu, J.B.

Li, S.W. Lin, Defective Ti₂Nb₁₀O_{27.1}: an advanced anode material for lithium-ion batteries, Sci. Rep. 5 (2015) 17836.

[S28]W.T. Mao, K.C. Liu, G. Guo, G.Y. Liu, K.Y. Bao, J.L. Guo, M. Hu, W.B. Wang,
B.B. Li, K.L. Zhang, Y.T. Qian, Preparation and electrochemical performance of Ti₂Nb₁₀O₂₉/Ag composite as anode materials for lithium ion batteries, Electrochim.
Acta 353 (2017) 396–402.

[S29]Q.F. Fu, J.R. Hou, R.H. Lu, C.F. Lin, Y. Ma, J.B. Li, Y.J. Chen, Electrospun $Ti_2Nb_{10}O_{29}$ hollow nanofibers as high-performance anode materials for lithium-ion batteries, Mater. Lett. 214 (2018) 60–63.

[S30]S.F. Lou, X.Q. Cheng, J.L. Gao, Q. Li, L. Wang, Y. Cao, Y.L. Ma, P.J. Zuo,Y.Z. Gao, C.Y. Du, H. Huo, G.P. Yin, Pseudocapacitive Li⁺ intercalation in porous

 $Ti_2Nb_{10}O_{29}$ nanospheres enables ultra-fast lithium storage, Energy Storage Mater. 11 (2018) 57–66.

[S31]X.M. Lou, C.F. Lin, Q. Luo, J.B. Zhao, B. Wang, J.B. Li, Q. Shao, X.K. Guo, N. Wang, Z.H. Guo, Crystal structure modification enhanced FeNb₁₁O₂₉ anodes for lithium-ion batteries, ChemElectroChem 4 (2017) 3171–3180.

[S32]C.F. Lin, L. Hu, C.B. Cheng, K. Sun, X.K. Guo, Q. Shao, J.B Li, N. Wang, Z.H. Guo, Nano-TiNb₂O₇/carbon nanotubes composite anode for enhanced lithium-ion batteries of electric vehicles, Electrochim. Acta 260 (2018) 65–72.