Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

## Supporting Information

## Design, synthesis and lithium-ion storage capability of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>

Qingfeng Fu<sup>a,b</sup>, Renjie Li<sup>b</sup>, Xiangzhen Zhu<sup>b</sup>, Guisheng Liang<sup>b</sup>, Lijie Luo<sup>b</sup>, Yongjun

Chen<sup>b</sup>, Chunfu Lin\*<sup>a,b</sup>, X.S. Zhao<sup>a,c</sup>

<sup>a</sup> Institute of Materials for Energy and Environment, School of Materials Science and

Engineering, Qingdao University, Qingdao 266071, China.

<sup>b</sup> School of Materials Science and Engineering, Hainan University, Haikou 570228,

China.

<sup>c</sup> School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane,

QLD 4072, Australia.

\* Corresponding author. E-mail address: linchunfu@qdu.edu.cn (C. Lin).



Fig. S1. Crystal structure of Nb<sub>16</sub>W<sub>5</sub>O<sub>55</sub>.



Fig. S2. Schematic sketch of *in-situ* XRD cell.



Fig. S3. (a) XRD pattern and (b) FESEM image of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.



Fig. S4. XRD patterns of Nb<sub>16</sub>W<sub>5</sub>O<sub>55</sub>.

The lattice constants of Nb<sub>16</sub>W<sub>5</sub>O<sub>55</sub> were refined to be a = 2.97083(42) nm, b = 0.38190(4) nm, c = 2.31409(39) nm and  $\beta = 126.546(6)^{\circ}$ . Its unit-cell volume was refined to be V = 2.10927(55) nm<sup>3</sup>.



Fig. S5. XPS spectra of (a) aluminum and (b) niobium elements in  $Al_{0.5}Nb_{24.5}O_{62}$ -M

and Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P.



Fig. S6. FESEM image of  $Al_{0.5}Nb_{24.5}O_{62}$ -M.



Fig. S7. FESEM image of precipitate after solvothermal reaction.



Fig. S8. (a) Nitrogen adsorption/desorption isotherm and (b) BJH desorption pore size

distribution of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P.



Fig. S9. (a) HRTEM image, (b) SAED pattern and (c) EDX elemental mapping

images of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-M.



Fig. S10. Electrochemical characterizations of  $Nb_{16}W_5O_{55}/Li$  cell: (a) CV curves at 0.2 mV s<sup>-1</sup>, (b) discharging/charging curves at 0.1C, (c) discharging/charging curves

at various current rates, (d) rate performance, (e) cyclability at 1C, and (f) long-term cyclability at 10C.



**Fig. S11.** Nyquist plots of  $Al_{0.5}Nb_{24.5}O_{62}$ -M/Li and  $Al_{0.5}Nb_{24.5}O_{62}$ -P/Li cells (*inset*: selected equivalent circuit), which were recorded in a frequency range of  $10^5$ - $10^{-2}$  Hz using a Zahner Zennium electrochemical workstation.

**Fig. S11** shows the Nyquist plots of the  $Al_{0.5}Nb_{24.5}O_{62}$ -M/Li and  $Al_{0.5}Nb_{24.5}O_{62}$ -P/Li cells. Each 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<sup>+</sup> desolvation, electron transfer and adsorption, which is denoted as the  $R_1$ /CPE<sub>1</sub> pair in the equivalent circuit (**Fig. S11** *inset*). The other semicircle observed in the medium-frequency region is associated with the Li<sup>+</sup> insertion at the  $Al_{0.5}Nb_{24.5}O_{62}$ -M/Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P particle surface (the  $R_2$ /CPE<sub>2</sub> pair). The slope observed in the low-frequency region corresponds to the Warburg resistance (W), representing the Li<sup>+</sup> diffusion in  $Al_{0.5}Nb_{24.5}O_{62}$ -M/Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P.  $R_b$  in the equivalent circuit embodies the Ohmic resistance of the cell, which is predominantly due to the electrolyte. The fitted  $R_1$  and  $R_2$  values for the

 $Al_{0.5}Nb_{24.5}O_{62}$ -M sample are 484 and 1117  $\Omega$ , respectively. In contrast, those for the  $Al_{0.5}Nb_{24.5}O_{62}$ -P sample were decreased to 170 and 712  $\Omega$ . Therefore, the  $Al_{0.5}Nb_{24.5}O_{62}$ -P sample exhibited faster Li<sup>+</sup> desolvation, electron-transfer, adsorption and Li<sup>+</sup> insertion at the active particle surface, indicating its faster electrochemical kinetics.



**Fig. S12.**  $Li^+$  diffusion coefficient ( $D_{Li}$ ) of Nb<sub>16</sub>W<sub>5</sub>O<sub>55</sub> calculated from GITT.



porous microspheres with high surface area

Fig. S13. Schematic structural feature of  $Al_{0.5}Nb_{24.5}O_{62}$ -P.



Fig. S14. (a) Pristine and two-dimensional *in-situ* XRD spectra of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-M/Li *in-situ* cell with corresponding first discharging curve within 3.0–0.8 V at 0.2C. (b) Variations in lattice constants of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub> (first discharging process).



Fig. S15. *Ex-situ* FESEM image of Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P electrode after 500 cycles at 10C.



**Fig. S16.** Electrochemical characterizations of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$  half cell: (a) CV curves at 0.2 mV s<sup>-1</sup>, (b) charging/discharging curves at 0.1C, (c) charging/discharging curves at various current rates, and (d) rate performance.



Fig. S17. CV curve of  $LiNi_{0.5}Mn_{1.5}O_4$ //Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P full cell at 0.2 mV s<sup>-1</sup>.



Fig. S18. Charging/discharging curves of  $LiNi_{0.5}Mn_{1.5}O_4$ //Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P full cell in

various cycles at 1C.



Fig. S19. Charging/discharging curves of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>//Al<sub>0.5</sub>Nb<sub>24.5</sub>O<sub>62</sub>-P full cell in

various cycles at 5C.



Fig. S20. (a) Discharging curves and (b) rate performance of

 $LiNi_{0.5}Mn_{1.5}O_4//Al_{0.5}Nb_{24.5}O_{62}$ -P full cell at 0 °C.

atom*	site	x	у	Z
M1	2a	0	0.25	0
M2	4c	0.1150	0	0.0138
M3	4c	0.2419	0	0.0595
M4	4c	0.3692	0	0.1148
M5	4c	0.4979	0	0.1652
M6	4c	0.0917	0	0.1879
M7	4c	0.2211	0	0.2364
M8	4c	0.3463	0	0.2872
M9	4c	0.4754	0	0.3374
M10	4c	0.0697	0	0.3631
M11	4c	0.1959	0	0.4140
M12	4c	0.3210	0	0.4619
M13	4c	0.4485	0	0.4485
01	4c	0.3819	0	0.0132
O2	4c	0.1814	0	0.0363
O3	4c	0.3157	0	0.0872
O4	4c	0.1024	0	0.1026
O5	4c	0.4358	0	0.1364
O6	4c	0.2366	0	0.1415
07	4c	0.0134	0	0.1380
O8	4c	0.3595	0	0.1978
09	4c	0.1487	0	0.2137
O10	4c	0.4922	0	0.2525
011	4c	0.2920	0	0.2633
O12	4c	0.0585	0	0.2734
O13	4c	0.4147	0	0.3074
O14	4c	0.2079	0	0.3503
O15	4c	0.3412	0	0.3815
O16	4c	0.1148	0	0.3981
O17	4c	0.4723	0	0.4336
O18	4c	0.2619	0	0.4402
O19	4c	0.0401	0	0.4627
O20	4c	0.3965	0	0.4851
O21	4c	0.1870	0	0.5037
O22	4c	0.3184	0	0.5651
O23	4c	0.4531	0	0.6209
O24	4c	-0.0017	0	0.6636
O25	4c	0.1373	0	0.7279
O26	4c	0.2647	0	0.7554
O27	4c	0.4244	0	0.8310
O28	4c	0.1276	0	0.9054
O29	4c	0.4866	0	0.9277
O30	4 <i>c</i>	0.2501	0	0.9761
O31	4c	0.0401	0	0.9815

**Table S1.** Fractional atomic parameters of  $Al_{0.5}Nb_{24.5}O_{62}$  with *C2* space group.

 $M = 0.02 A l^{3+} + 0.98 N b^{5+}$ 

sample	potential at cathodic peak (V)	potential at anodic peak (V)	potential difference (V)
$\begin{array}{c} Al_{0.5}Nb_{24.5}O_{62}\text{-}M\\ (Nb^{4+}\!/Nb^{5+}) \end{array}$	1.606	1.756	0.150
$\begin{array}{c} Al_{0.5}Nb_{24.5}O_{62}\text{-}P\\ (Nb^{4+}\!/Nb^{5+}) \end{array}$	1.616	1.744	0.128
$\begin{array}{c} Al_{0.5}Nb_{24.5}O_{62}\text{-}M\\ (Nb^{3+}\!/Nb^{4+}) \end{array}$	1.198	1.386	0.188
$\begin{array}{c} Al_{0.5}Nb_{24.5}O_{62}\text{-}P\\ (Nb^{3+}\!/Nb^{4+}) \end{array}$	1.130	1.307	0.177

**Table S2.** Potentials at cathodic/anodic CV peaks and potential differences of $Al_{0.5}Nb_{24.5}O_{62}$ -M/Li and  $Al_{0.5}Nb_{24.5}O_{62}$ -P/Li cells at 0.2 mV s<sup>-1</sup> (2<sup>nd</sup> cycle).

## References

[S1]M. Nakayama, H. Ikuta, Y. Uchimoto, M. Wakihara, J. Phys. Chem. B, 2003, 107, 10603.