## **Supporting Information**

## LiTa<sub>2</sub>PO<sub>8</sub>: A Fast Lithium-ion Conductor with New Framework Structure

Jaegyeom Kim,<sup>a</sup> Juhyun Kim,<sup>a</sup> Maxim Avdeev,<sup>bc</sup> Hoseop Yun,<sup>a</sup> and Seung-Joo Kim\*<sup>a</sup>

<sup>a</sup> Department of Energy Systems Research and Department of Chemistry, Ajou University, Suwon 16499, Republic of Korea <sup>b</sup> Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

<sup>c</sup> School of Chemistry, The University of Sydney, Sydney 2006, Australia

\*Corresponding Author: sjookim@ajou.ac.kr

## **Experimental Section**

Synthesis: LiTa<sub>2</sub>PO<sub>8</sub> was synthesized via a conventional solid-state reaction of Li<sub>2</sub>CO<sub>3</sub> (Sigma Aldrich,  $\geq$ 99.0%), Ta<sub>2</sub>O<sub>5</sub> (Sigma Aldrich, 99%), and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Sigma Aldrich,  $\geq$ 98%). An excess of Li<sub>2</sub>CO<sub>3</sub> (10 mol%) was added to compensate for the loss of lithium during high-temperature annealing. The powders were mixed well and preheated under three conditions: (i) heat treatments at 600 °C for 8h and 1000°C for 8h (sample **A**), (ii) heat treatments at 600 °C for 8h and 900 °C for 8h (sample **B**), and (iii) heat treatments at 600 °C for 8h (sample **C**). Each reaction product was ball-milled for 1h with toluene in a jar using zirconia balls (Pulverisette 7, Fritsch GmbH, Idar–Oberstein, Germany). After ball-milling, the powders were pressed into pellets and sintered at 1050 °C for 12 h. The pellets were covered with the corresponding powders to prevent lithium loss during sintering. The relative densities of the sintered pellets were 96.6% (sample **A**), 93.4% (sample **B**), and 89.4% (sample **C**). The morphology of the sintered pellets was monitored using a scanning electron microscope (SEM) (JSM-6700F, JEOL, Seoul, Tokyo Japan).

Diffraction Data Collection: Powder X-ray diffraction measurement was performed using a Rigaku DMAX2200PC X-ray diffractometer equipped with a graphite monochromator ( $\lambda = 1.5418$  Å). Synchrotron X-ray powder diffraction (SXPD) data were collected at the 9B beamline of the Pohang Light Source, Pohang Accelerator Laboratory, Korea, in the 2 $\theta$  range of 10–125° with a step size of 0.005° using a double-crystal Si (111) monochromator with a wavelength of 1.4861 Å. Neutron powder diffraction (NPD) was performed using the Echidna powder diffractometer at the Australian Nuclear Science and Technology Organisation's OPAL facility. The NPD data of the powder sample loaded in a vanadium can were collected with a wavelength of 1.622 Å over the 2 $\theta$  range of 6–162° at a step size of 0.05°. The neutron scattering coherence lengths, *b* (in fm), used were Li (-1.90), Ta (6.91), P (5.13), and O (5.803).<sup>1</sup>

*Structure Determination*: The crystal structure of LiTa<sub>2</sub>PO<sub>8</sub> was determined *ab initio* from the powder diffraction data. The EXPO2014 program<sup>2</sup> was used to index peaks determine lattice parameters and space group from the synchrotron data. The initial structure model (except for Li) was deduced by SXPD by applying the direct method. The model was implemented to the neutron diffraction data analysis, and difference Fourier maps were calculated to determine the Li atom positions using the GFOURIER program.<sup>3</sup> The final structure was obtained by a combined Rietveld refinement using the FullProf program (Version 6.10),<sup>4,5</sup> in which the NPD and SXPD data were given the weights 0.8 and

0.2. The diffraction profile was fitted with the Thompson-Cox-Hastings pseudo-Voigt function and manually selected background points.<sup>6</sup> The final refinement involved the following parameters: scale factor, unit-cell parameters, pseudo-Voigt parameters for the peak-shape function, asymmetry parameter, occupancy factors for lithium, and positional parameters and isotropic temperature factors for lithium, tantalum, phosphorus, and oxygen. The synchrotron refinement contains a small amount (~3.6 wt%) of LiTa<sub>3</sub>O<sub>8</sub> impurities. Bond Valence Energy Landscape (BVEL) was calculated according to the method developed by Adams<sup>7</sup> using the BondStr software in the FullProf suite,<sup>5</sup> and BVEL maps were calculated considering anionic neighbors up to 8 Å for Li ion.

Conductivity Measurements: A.C. impedance measurements were performed using an impedance analyzer (HP 4192A, Hewlett-Packard, Palo Alto, CA) in the frequency range from 5 Hz to 13 MHz (with an amplitude of 10 mV). Two Au layers were used as ion-blocking electrodes. The Au paste was brush-painted on both sides of the pellet and fired at 700°C for 1 h. Variable temperature conductivity measurements were carried out in the temperature range of 4–200 °C. Prior to each impedance measurement, the samples were equilibrated at a constant temperature for least 2 h. The impedance spectra were fitted with equivalent circuits using the ZView program.<sup>8</sup> In addition, the electronic conductivity ( $\sigma_e$ ) was evaluated from D.C. potentiostatic polarization measurements performed by applying a constant potential of 1.0 V on the Au/LiTa<sub>2</sub>PO<sub>8</sub>/Au symmetric cell for 3600 s. The value of  $\sigma_e$  was calculated from the following equation:

$$\sigma = \frac{lU}{AI}$$

where U is the polarization voltage, l is the thickness of the electrolyte, A is the area of the Au electrode, and I is the current, respectively.

*Cyclic Voltammetry*: To investigate the electrochemical stability of LiTa<sub>2</sub>PO<sub>8</sub>, cyclic voltammetry was performed. In this test, two cathodes with and without LiTa<sub>2</sub>PO<sub>8</sub> powder were prepared. The LiTa<sub>2</sub>PO<sub>8</sub>-free electrode was composed of 80 wt% conductive carbon and 20 wt% polyvinylidene (PVDF), while the LiTa<sub>2</sub>PO<sub>8</sub>-containing electrode was composed of 80 wt% LiTa<sub>2</sub>PO<sub>8</sub>, 15 wt% conductive carbon, and 5 wt% PVDF. The materials were mixed in 1-methyl-2-pyrrolidinone (NMP), coated onto a copper foil, and dried at 120 °C overnight. Coin cells were assembled using the cathode, a lithium foil as the anode, Celgard 2400 as the separator, and 1 M LiPF<sub>6</sub> in a solution of ethylene carbonate/dimethyl carbonate (EC/DMC, 1/1 by volume) as the electrolyte. Cyclic voltammetry was performed at a rate of 0.5 mV s<sup>-1</sup> using a potentiostat/galvanostat (WBCS3000, WonAtech, Seoul, South Korea).

Radiation	NPD		SXRD
Empirical formula		LiTa <sub>2</sub> PO <sub>8</sub>	
Formula weight $(M_r)$		527.81	
Space group		C2/c	
Z		8	
Density (g/cm <sup>3</sup> )		5.848	
Temperature (K)		298	
Wavelength (Å)	1.6220		1.5173
2θ range (°)	6–162		10–125
2θ step (°)	0.05		0.005
No. of reflections	1139		1030
No. of data	3194		23095
No. of refine parameters		96	
<i>a</i> (Å)		9.71545(2)	
<i>b</i> (Å)		11.53580(2)	
<i>c</i> (Å)		10.69708(3)	
$\beta$ (°)		90.0355(3)	
Volume (Å <sup>3</sup> )		1198.88(1)	
$R_p$	4.58		10.7
$R_{wp}$	5.95		14.1
$R_{exp}$	2.81		9.76
<i>R</i> <sub>Bragg</sub>	4.46		9.78
$\chi^2$	4.49		2.10
$\rho_{\min./max.}$ residuals	-0.02/0.03		-1.71/2.63

**Table S1**. Summary of structural information of LiTa<sub>2</sub>PO<sub>8</sub> determined by the combined synchrotron X-ray powder diffraction (SXPD) and neutron powder diffraction (NPD).

Table S2. Atomic parameters and isotropic temperature factors for LiTa<sub>2</sub>PO<sub>8</sub>.

Atom	Wyckoff Site	s.o.f.	x	у	Ζ	$B_{\rm iso}$ (Å <sup>2</sup> )
Ta1	8 <i>f</i>	1	0.2456(2)	0.0957(1)	0.2555(3)	0.34(3)
Ta2	4 <i>e</i>	1	0	0.3463(2)	1/4	0.31(4)
Ta3	4a	1	0	0	0	0.30(4)
Р	8 <i>f</i>	1	0.4993(7)	0.2097(4)	0.0596(4)	0.56(6)
01	8 <i>f</i>	1	0.0569(6)	0.3343(5)	0.0677(5)	1.22(9)
O2	8 <i>f</i>	1	0.3817(5)	0.1371(5)	0.4061(5)	1.05(9)
O3	8 <i>f</i>	1	0.3582(7)	0.5064(5)	0.1271(5)	1.27(8)
O4	8 <i>f</i>	1	0.0475(6)	0.1645(5)	0.5497(5)	1.05(9)
O5	8 <i>f</i>	1	0.1443(6)	0.2342(4)	0.2879(4)	0.81(8)
O6	8 <i>f</i>	1	0.1379(6)	0.0567(5)	0.1161(5)	1.47(9)
O7	8 <i>f</i>	1	0.3787(6)	0.2023(5)	0.1537(5)	1.3(1)
O8	8 <i>f</i>	1	0.1368(7)	0.4655(5)	0.2824(4)	1.4(1)
Li1	8 <i>f</i>	0.72(3)	0.246(2)	0.357(2)	0.140(2)	$1.6(4)^{[a]}$
Li2	8 <i>f</i>	0.21(3)	0.112(8)	0.387(7)	0.401(7)	$1.6(4)^{[a]}$
Li3	4 <i>b</i>	0.14(2)	1/2	0	0	1.6(4) <sup>[a]</sup>

[a] The temperature factors of lithium atoms are constrained to be equal.

Temperature (°C)	$\sigma_{\rm b}({ m S}{ m cm}^{-1})$	$\sigma_{ m gb}~({ m S~cm}^{-1})$	$\sigma_{\rm total} ({ m S} { m cm}^{-1})$
4	$5.38 \times 10^{-4}$	$6.58  imes 10^{-5}$	$5.86 \times 10^{-5}$
17	$1.08 \times 10^{-3}$	$1.69 \times 10^{-4}$	$1.46  imes 10^{-4}$
25	$1.63 \times 10^{-3}$	$2.92 \times 10^{-4}$	$2.48  imes 10^{-4}$
32	$2.19 \times 10^{-3}$	$4.44  imes 10^{-4}$	$3.69 \times 10^{-4}$
40	$2.97 \times 10^{-3}$	$6.79  imes 10^{-4}$	$5.52  imes 10^{-4}$
47	$3.98 \times 10^{-3}$	$1.02 \times 10^{-3}$	$8.11  imes 10^{-4}$
54	$5.29 \times 10^{-3}$	$1.57 \times 10^{-3}$	$1.21 \times 10^{-3}$
63	$6.37 \times 10^{-3}$	$2.44 \times 10^{-3}$	$1.76 \times 10^{-3}$
72	$8.67 \times 10^{-3}$	$3.31 \times 10^{-3}$	$2.40 \times 10^{-3}$
82	$1.09 \times 10^{-2}$	$4.57 \times 10^{-3}$	$3.22 \times 10^{-3}$
90	$1.40 \times 10^{-2}$	$6.09 \times 10^{-3}$	$4.24 \times 10^{-3}$
103	-	-	$6.88 \times 10^{-3}$
117	-	-	$1.03 \times 10^{-2}$
135	-	-	$1.57 \times 10^{-2}$
159	-	-	$2.47 \times 10^{-2}$
180	-	-	$3.37 \times 10^{-2}$
200	-	-	$4.40 \times 10^{-2}$

Table S3. Bulk, grain boundary and total conductivities of  $LiTa_2PO_8$  (sample A) measured in the heating cycle.

Table S4. Conductivities and capacitances<sup>[a]</sup> data of LiTa<sub>2</sub>PO<sub>8</sub> with different relative densities at 17 °C.

Relative density (%)	$\sigma_{ m b}~({ m S~cm^{-1}})$	$C_{b}(\mathrm{F})$	$\sigma_{ m gb}({ m S}{ m cm}^{-1})$	$C_{\rm gb}\left({ m F} ight)$	$\sigma_{ m total}({ m S}~{ m cm}^{-1})$
96.6 <sup>[b]</sup> (sample A)	$1.11 \times 10^{-3}$	$9.98 \times 10^{-12}$	$1.85  imes 10^{-4}$	$4.95 \times 10^{-9}$	$1.59 \times 10^{-4}$
93.4 <sup>[c]</sup> (sample <b>B</b> )	$1.10 \times 10^{-3}$	$2.93 \times 10^{-12}$	$7.66 \times 10^{-5}$	$7.32 \times 10^{-9}$	$7.16 \times 10^{-5}$
89.4 <sup>[d]</sup> (sample C)	$7.68  imes 10^{-4}$	$1.02  imes 10^{-10}$	$5.93 \times 10^{-5}$	$8.89 \times 10^{-9}$	$5.50 \times 10^{-5}$

[a] The conductivity of the sample was calculated by the following equation:  $\sigma = l/(A \cdot R)$ , where *l* is the thickness of the electrolyte, *A* is the area of the Au electrode, and *R* is resistance, respectively. The subscripts b and gb refer to the bulk and grain boundary, respectively. [b] 0.21 cm thickness and 1.05 cm diameter. [c] 0.22 cm thickness and 1.08 cm diameter. [d] 0.21 cm thickness and 1.16 cm diameter.

Ta1–O2	2.137(6)	Ta2–O1 (×2)	2.032(5)	P-01	1.552(7)
Ta1–O3	1.912(6)	Ta2–O5 (×2)	1.950(5)	PO2	1.473(8)
Tal-O5	1.908(5)	Ta2–O8 (×2)	1.943(6)	P04	1.530(8)
Tal-O6	1.876(6)			Р-07	1.547(8)
Ta1–O7	2.091(6)	Ta3–O3 (×2)	1.938(6)		
Ta1–O8	1.930(6)	Ta3–O4 (×2)	2.024(6)		
		Ta3–O6 (×2)	1.940(6)		
Li1–O1	2.00(2)	Li2–O1	1.78(8)	Li3–O1 (×2)	2.117(6)
Li1–O3	2.05(2)	Li2–O2	2.09(8)	Li3–O2 (×2)	2.198(5)
Li1–O5	2.34(2)	Li2–O5	2.15(8)		
Li1–O7	2.21(2)	Li2-08	1.57(8)		
Li1–O8	2.23(2)				
O2–Ta1–O3	87.2(4)	O1-Ta2-O1	172.2(5)	O3–Ta3–O3	180.0(6)
O2–Ta1–O5	89.7(4)	O1–Ta2–O5 (×2)	87.6(4)	O3–Ta3–O4	89.2(4)
O2–Ta1–O6	175.7(5)	O1–Ta2–O8	91.9(4)	O3–Ta3–O4	90.8(4)
O2-Ta1-O7	83.0(4)	O1-Ta2-O8	93.6(4)	O3–Ta3–O6	91.7(5)
O2-Ta1-O8	88.1(4)	O1–Ta2–O5 (×2)	87.2(4)	O3–Ta3–O6 (×2)	88.3(4)
O3–Ta1–O5	93.4(4)	O1-Ta2-O8	93.6(4)	O3–Ta3–O4	90.8(4)
O3–Ta1–O6	95.7(4)	O1-Ta2-O8	91.9(4)	O3–Ta3–O4	89.2(4)
O3–Ta1–O7	170.2(5)	O5–Ta2–O5	96.9(4)	O3–Ta3–O6	91.7(5)
O3–Ta1–O8	91.8(5)	O5–Ta2–O8 (×2)	86.6(4)	O4–Ta3–O4	180.0(5)
O5–Ta1–O6	93.3(4)	O5–Ta2–O8 (×2)	176.3(5)	O4–Ta3–O6 (×2)	90.5(4)
O5–Ta1–O7	85.5(4)	O8–Ta2–O8	89.9(5)	O4–Ta3–O6 (×2)	89.5(4)
O5–Ta1–O8	174.2(5)			O6–Ta3–O6	180.0(5)
O6–Ta1–O7	94.1(4)				
O6-Ta1-O8	88.6(4)				
O7–Ta1–O8	89.0(4)				
O1–P–O2	108.0(6)	Ol-Lil-O3	125.0(10)	01–Li2–O2	78(3)
O1–P–O4	110.9(6)	01–Li1–O5	78.5(8)	01–Li2–O5	88(3)
O1–P–O7	106.7(6)	01–Li1–07	117.1(9)	01–Li2–08	120(4)
O2–P–O4	108.4(7)	01–Li1–08	84.7(9)	02–Li2–O5	116(3)
O2–P–O7	113.7(6)	03–Li1–O5	141.2(9)	02–Li2–O8	150(4)
O4–P–O7	109.2(6)	03–Li1–07	111.6(9)	O5–Li2–O8	90(4)
		03–Li1–08	80.1(9)	o	100.0/=
		05–Li1–07	73.3(8)	01–Li3–01	180.0(5)
		05–Li1–08	71.4(8)	O1–Li3–O2 (×2)	110.9(4)
		07–Li1–O8	133.1(9)	01–Li3–O2 (×2)	69.1(3)
				02-Li3-O2	180.0(4)

Table S5. Selected interatomic distances (Å) and angles (°) for  $LiTa_2PO_8$ .

Atom	CN	BVS <sup>[a]</sup> (v.u.)	Atom	CN	$\mathrm{BVS}^{[a]}\left(\mathrm{v.u.}\right)$
Tal	6	5.34(4)	01	5	2.21(3)
Ta2	6	5.20(3)	O2	4	2.09(3)
Ta3	6	5.31(3)	O3	3	2.12(3)
			O4	2	2.02(3)
Р	4	5.14(5)	O5	4	2.06(2)
			O6	2	2.07(2)
Li1	5	0.80(2)	O7	3	1.93(3)
Li2	4	1.5(2)	O8	4	2.16(4)
Li3	4	0.62(1)			
					$GH^{[b]} = 0.24$ v.u.

**Table S6**. The coordination numbers (CN), bond valence sums (BVS), and global instability index (GII) for LiTa<sub>2</sub>PO<sub>8</sub>.

[a]  $V_i = \sum_j \exp\{(d_{ij} - R_0)/0.37\}$ , [b]  $GII = \langle \sum_i (\Delta V_i)^2 \rangle^{1/2}$ 



Fig. S1. Powder diffraction pattern of LiTa<sub>2</sub>PO<sub>8</sub> as measured by conventional laboratory powder XRD.



**Fig. S2**. Difference Fourier maps plotted for z = 0.14, 0.41 and 0, obtained from the refinement of the NPD patterns of the LiTa<sub>2</sub>PO<sub>8</sub> by taking into account solely the  $[Ta_2PO_8]^{-1}$  framework. The blue domains represent to the negative value and correspond to the positions of the missing lithium ions.



**Fig. S3.** Impedance plots of the heating cycle at different temperatures. (a) 4–17 °C (b) 25–40 °C (c) 47–82 °C (d) 90–135 °C (e) 159–200 °C. The measured and fitted data are plotted using blank points and solid lines, respectively. The inset figures indicate the equivalent circuit models used for fitting analysis. In the equivalent circuit, L, R, and CPE for inductance, resistance, and constant phase element, respectively. The subscripts b, gb, int, and el refer to bulk, grain boundary, sample-electrode interface, and electrode contributions, respectively. The capacitances were calculated to have the magnitudes in the order of 10 pF (bulk), 1 nF (grain boundary), and 100 nF (sample-electrode interface), which are consistent with the values of the typical ion conducting oxides reported in the literature.<sup>9</sup> The inductances L were estimated to be in the range of 0.58–0.81  $\mu$ H.



**Fig. S4**. SEM images of the pellet surface of LiTa<sub>2</sub>PO<sub>8</sub>. Small pores (indicated by arrows) are detected in the low-density pellets (samples **B**, **C**).



Fig. S5. D.C. polarization curves of  $LiTa_2PO_8$  at 1 V polarization voltage using blocking Au electrodes.



**Fig. S6.** First five cyclic voltammograms curves. (a)  $LiTa_2PO_8$ -containing electrode. (b)  $LiTa_2PO_8$ -free electrode. The steps below 0.8 V appeared in both samples are attributed to the formation of a thin solid electrolyte interface (SEI) layers on the conductive carbon particles due to decomposition of the electrolyte at low potential.<sup>10</sup> The peak observed in the range from 1.5 to 0.8 V in (a) may be due to the reduction of  $LiTa_2PO_8$  by lithium.

## **References for the supporting information**

- 1 V. F. Sears, *Neutron news*, 1992, **3**, 26-37.
- 2 A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Crystallogr.*, 2013, **46**, 1231-1235.
- 3 J. González-Platas and J. Rodriguez-Carvajal, Univ. La Laguna, Tenerife, Spain, 2002.
- 4 J. Rodríguez-Carvajal, Physica B: Condensed Matter, 1993, 192, 55-69.
- 5 J. Rodríguez-Carvajal, Commission on powder diffraction (IUCr). Newsletter, 2001, 26, 12-19.
- 6 P. Thompson, D. Cox and J. Hastings, J. Appl. Crystallogr., 1987, 20, 79-83.
- 7 S. Adams, Solid State Ionics, 2006, 177, 1625-1630.
- 8 D. Johnson, Inc., Southern Pines, NC, 2002, 200.
- 9 J. T. Irvine, D. C. Sinclair and A. R. West, Adv. Mater., 1990, 2, 132-138.
- 10 C. Chen and K. Amine, Solid State Ionics, 2001, 144, 51-57.