Supplementary Information

A New Polymorph of Lithium Manganese Pyrophosphate β-$Li_2MnP_2O_7$

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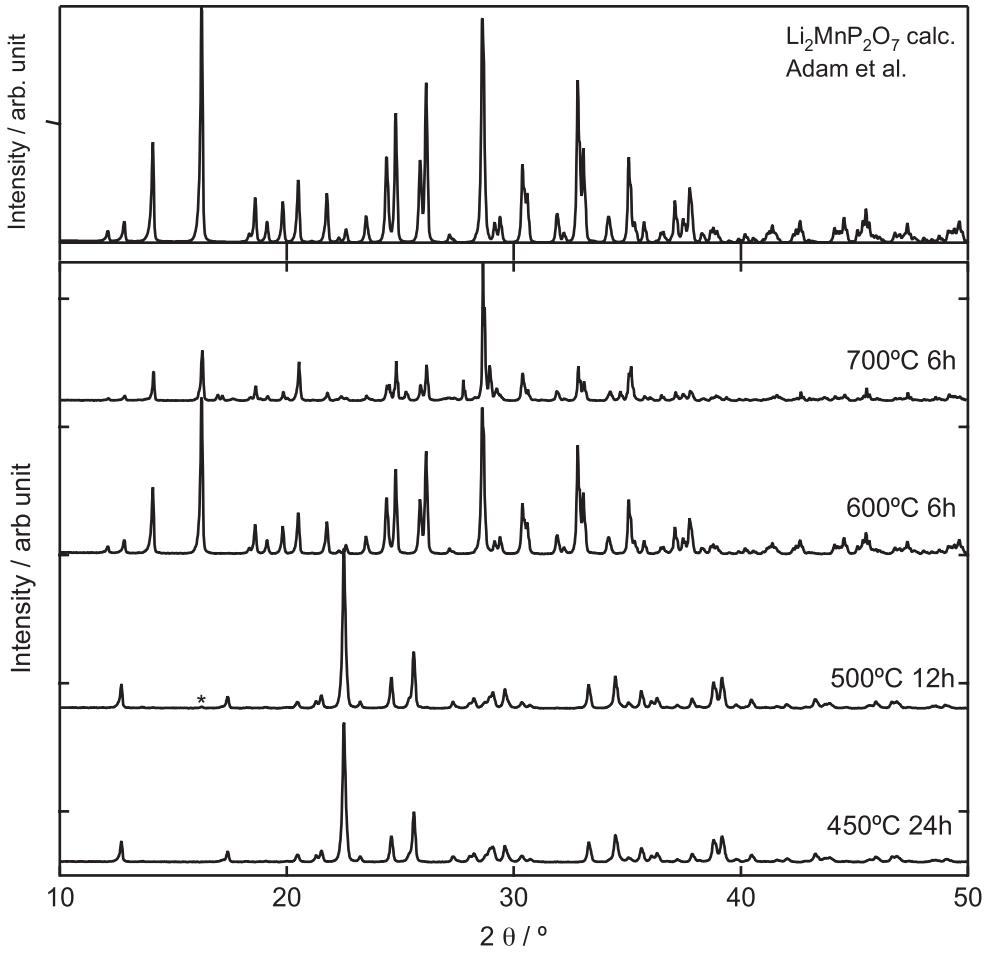

Figure S1 Powder X-ray diffraction patterns of the $Li_2MnP_2O_7$ samples.

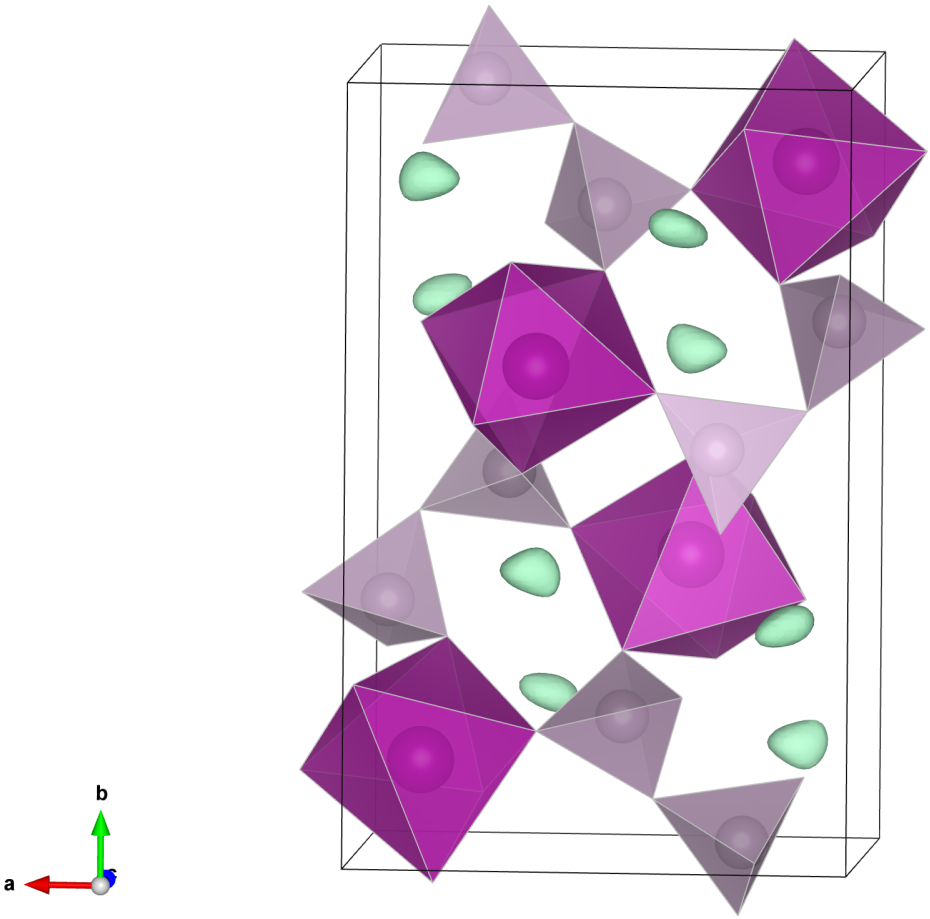

Figure S2 Isosurface of difference Fourier synthesis map drown with $[MnP_2O_7]^{2-}$ framework structure. The isosurface value is 0.7 $Å^{-3}$. The map was calculated without lithium to determine the lithium positions. This figure is drown with a computer program VESTA (K. Momma et al., *J. Appl. Cryst.*, 41(3): 653–658)

Table S1 Details of XRD data collection

Crystal data	
Chemical formulae	$Li_2MnP_2O_7$
M_r	242.76
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature	293 K
a	8.2522(2)
b	12.9533(3)
c	4.98188(12)
β	92.8282(14)
V	531.88(2)
Z	4
Radiation type	Cu $K\alpha$, λ = 1.5406, 1.5444 Å
Detector	NaI scintillation counter
Monochromator	Diffracted beam curved graphite
Specimen shape, size	Flat plate, 15 mm × 20 mm

Data collection	
Specimen mounting	borosilicate glass holder
Data collection mode	Reflection
Scan Method	Step
$2\theta_{min}$, $2\theta_{max}$ (°)	10, 100
2θ step size	0.02°

Table S2 Fractional coordinates for b-$Li_2MnP_2O_7$ refined by Rietveld analysis.

Atom	*x*	*y*	*z*	*B* / Å^2
Mn	0.3598(2)	0.37040(13)	0.7278(4)	0.99(5)
P1	0.9580(3)	0.3097(2)	0.6876(6)	0.86(7)
P2	0.7239(3)	0.4710(2)	0.7643(5)	0.71(7)
O1	0.7402(7)	0.5719(4)	0.9092(11)	0.73(6)
O2	0.6098(6)	0.3943(4)	0.8926(11)	=O1
O3	0.6793(6)	0.4835(4)	0.4667(10)	=O1
O4	0.9038(6)	0.4196(4)	0.7945(10)	=O1
O5	0.9752(7)	0.2378(4)	–0.0676(11)	=O1
O6	0.8250(7)	0.2738(4)	0.4812(11)	=O1
O7	0.1202(7)	0.3238(4)	0.5627(10)	=O1
Li1	0.666(2)	0.3551(12)	0.282(3)	1.0
Li2	0.648(2)	0.1945(13)	0.696(3)	1.0

Table S3 Bold valence sum (BVS).

Atom	BVS	Formal Charge
Mn	1.94	+2
P1	4.89	+5
P2	4.93	+5
O1	2.10	–2
O2	1.80	–2
O3	1.99	–2
O4	2.04	–2
O5	1.84	–2
O6	1.99	–2
O7	1.99	–2
Li1	0.98	+1
Li2	1.00	+1

Table S4 Selected bond length.

		Bond length / Å
Mn—	O1	2.1580(56)
	O2	2.2076(52)
	O3	2.1493(53)
	O5	2.2722(56)
	O6	2.2871(54)
	O7	2.1923(56)
P1—	O1	1.4896(57)
	O2	1.5189(53)
	O3	1.5338(57)
	O4	1.6304(56)
P2—	O4	1.5898(56)
	O5	1.5379(58)
	O6	1.5329(57)
	O7	1.5153(62)
Li1—	O2	2.027(18)
	O3	1.904(17)
	O5	2.174(18)
	O6	1.905(17)
Li2—	O1	1.893(18)
	O5	2.105(18)
	O6	2.117(18)
	O7	1.867(17)

Table S5 Selected bond angle (º).

Mn	O1	O2	O3	O5	O6	O7
O1	-	91.8(2)	90.9(2)	89.1(2)	92.6(2)	87.8(2)
O2	91.8(2)	-	171.8(2)	108.3(2)	76.1(2)	99.4(2)
O3	90.9(2)	171.8(2)	-	84.9(2)	85.2(2)	92.1(2)
O5	89.1(2)	108.3(2)	84.9(2)	-	162.6(2)	160.8(2)
O6	92.6(2)	76.1(2)	85.2(2)	162.6(2)	-	81.3(2)
O7	87.8(2)	99.4(2)	92.1(2)	160.8(2)	81.3(2)	-

P1	O1	O2	O3	O4
O1	-	110.3(3)	113.6(3)	105.1(3)
O2	110.3(3)	-	114.4(3)	104.8(3)
O3	113.6(3)	114.4(3)	-	107.9(3)
O4	105.1(3)	104.8(3)	107.9(3)	-

P2	O4	O5	O6	O7
O4	-	107.5(3)	110.8(3)	106.7(3)
O5	107.5(3)	-	106.7(3)	112.9(3)
O6	110.8(3)	106.7(3)	-	111.9(3)
O7	106.7(3)	112.9(3)	111.9(3)	-

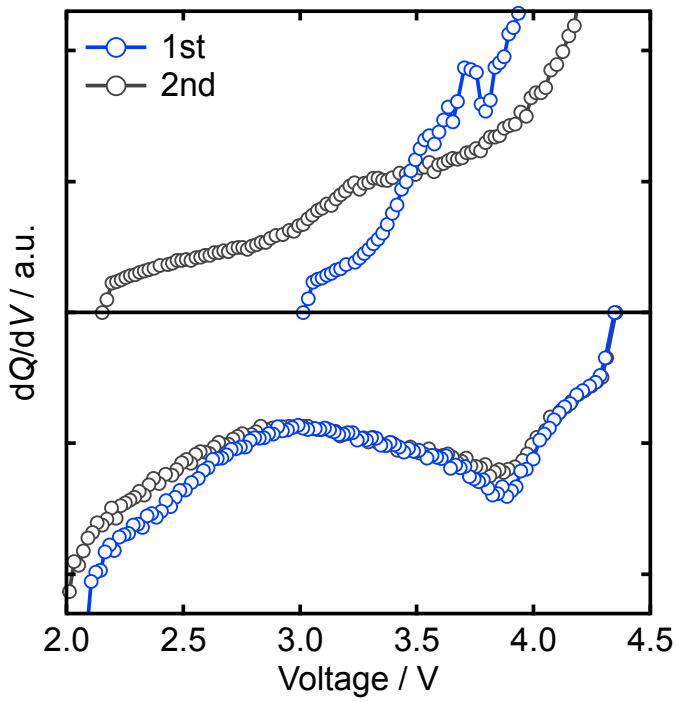

Figure S3 Incremental capacity dQ/dV versus the cell voltage. Upper and lower show the charging and the discharging process respectively.

Table S6 Reaction potential of $Li_2MP_2O_7$-type and $LiMPO_4$-type compounds versus lithium (V).

Structure	$LiMPO_4$	α-$Li_2MP_2O_7$	β-$Li_2MP_2O_7$
Mn	4.1[1]	4.45[4]	~3.9 (this work)
Fe	3.4[2]	3.5[5] (3.9 with Mn)[6]	-
Co	4.7[3]	4.9[7]	-

1. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* **144** (1997), 1188–1194.

2. Guohua Li, Hideto Azuma, and Masayuki Tohda, *Electrochem. Solid-State Lett.* **5** (2002), A135–A137.

3. K. Amine, H. Yasuda, and M. Yamachi, *Electrochem. Solid-State Lett.* **3** (2000), 178–179.

4. M. Tamaru, P. Barpanda, Y. Yamada, S. Nishimura, and A. Yamada, *J. Mater. Chem.* **22** (2012), 24526–24529.

5. S. Nishimura, M. Nakamura, R. Natsui, and A. Yamada, *J. Am. Chem. Soc.* **132** (2010), 13596–13597.

6. N. Furuta, S. Nishimura, P. Barpanda, and A. Yamada, *Chem. Mater.* **24** (2012), 1055–1061.

7. H. Kim, S. Lee, Y. Park, H. Kim, J. Kim, S. Jeon, and K. Kang, *Chem. Mater.* **23** (2011), 3930–3937.