Supporting Information

A New Polymorph of $Na_2MnP_2O_7$ as a 3.6 V Cathode Material for Sodium-ion Batteries

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Calculation & Experimental Details:

***Computational Method*:** All the first principle calculations were performed with the Vienna *ab initio* simulation package *VASP*.[1] The core electrons were treated with the projector augmented wave method as implemented in the *VASP* code. The GGA exchange-correlation functional employed was due to Perdew, Burke, and Ernzerhof (PBE). Rotationally invariant, spherically averaged version of Hubbard-type correction (+U) was used to characterize the local electrons. We employed effective coulomb energy U = 4.2 for the Fe atom. For the planewave expansion of wave function a cutoff of 520 eV was used. Integration over the Brillouin zone was performed with a Monkhorst-Pack k-point mesh of 2x2x2. For singly sodiated structure $NaMnP_2O_7$, ordering of sodium within a unit cell of 8 formula units were considered. The derivative structures were generated and the 15 structures with the lowest electrostatic energies were then computed with *ab initio* method, the resulting lowest energy structure was employed for voltage calculation according to:

$$\text{Voltage} = [\, E(NaMnP_2O_7) + E(Li) \,] - E(Na_2MnP_2O_7)$$

***Material Synthesis*:** The β-$Na_2MnP_2O_7$ polymorph was prepared by conventional solid-state synthesis using a stoichiometric mixture of NaH_2PO_4 (Wako, 99%) and MnC_2O_4 (Kojundo, 99+%). The precursors were intimately mixed by wet planetary ball-milling in acetone media for 3 h (600 rpm) employing Cr-hardened stainless steel (Cr-SS) milling media and container. The precursor mixture was then pressed into pellets, quickly ramped up to 600 °C (rate = 10 °C/min) and were sintered for 6~12 h in a tubular furnace under steady argon flow to obtain the desired phase.

Alternately, the β-$Na_2MnP_2O_7$ polymorph was prepared by solution combustion synthesis[1] by dissolving stoichiometric amounts of NaH_2PO_4 and $Mn(CH_3COO)_2.4H_2O$ (Wako, 99.9%) or $Mn(NO_3)_2.6H_2O$ (Sigma-Aldrich, 99%) with citric acid ($C_6H_8O_7$) (Wako, 98%) as combustion agent. Continuous heating (at 120 °C) of this solution led to the formation of an amorphous intermediate complex, which was later annealed at 600 °C for 1~6 h under steady argon flow to obtain the end product. Combustion route is capable of yielding the final product by a quick 1-minute annealing, but longer annealing was performed to improve crystallinity. Further, combustion synthesis leads to the one-step formation of nanoscale carbon-coated product.[2]

***Structural Analysis*:** X-ray diffraction patterns of polycrystalline $Na_2MnP_2O_7$ powders were acquired by a Rigaku RINT-TTR III powder diffractometer (operating at 50 kV, 300 mA) equipped with a Cu Kα source (λ_1 = 1.54056 Å, λ_2 = 1.54439 Å). A typical scan was performed in the 2θ range of 5~80° (step size = 0.03°.sec^{-1}). Full powder pattern matching and Rietveld refinement were performed using FullProf software.[3]

***Physical Analyses*:** Scanning electron micrographs were obtained on combustion synthesized $Na_2MnP_2O_7$ powder sample mounted on conducting carbon paste using a Hitachi S-4800 SEM unit operating at 2 kV. Infra-red spectroscopy was conducted using a JASCO FT/IT-6300 FTIR instrument over the range 400~4000 cm^{-1}. Typically, an average of 32 scans were obtained (step size = 4.0 cm^{-1}). Thermal analysis was performed with a Seiko EXSTAR 6000 instrument in the temperature range of 25~800 °C at a moderate heating rate of 5° C/min.

***Electrochemical Analyses*:** For electrochemical measurements, the working electrode (cathode) was formulated by mixing combustion-synthesized $Na_2MnP_2O_7$, acetylene carbon black and polyvinylidene difluoride (PVdF) in w/w ratio of 70/20/10. This working electrode composite was pressed on an Al mesh working as the current collector, with an average cathode loading of 3 mg/cm^2. Coin cells were assembled inside an Ar-filled glove box by taking the cathode film as the working electrode, Na metal foils as counter electrode and 1 M $NaClO_4$ dissolved in propylene carbonate (PC) acting as electrolyte. The electrolyte (trade name: LIPASTE-P/S1) was commercially procured from Tomiyama High Purity Chemicals Ltd. (Tokyo, Japan). Galvanostatic cycling was conducted in the voltage range 2 ~ 4.5 V at a rate of C/20 (at 25 °C).

References:

1. Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
2. Barpanda, P.; Ye, T.; Chung, S.C.; Yamada, Y.; Nishimura, S.; Yamada, A. *J. Mater. Chem.* **2012**, *22*, 13455.
3. Rodriguez-Carvajal, J. *Physica B* **1993**, *192*, 55.

Table S1. Crystallographic data of β-$Na_2MnP_2O_7$ polymorph derived from the Rietveld refinement of the X-ray powder diffraction pattern acquired at room temperature. The lattice parameters, atomic coordinates and equivalent isotropic displacement coefficients of $Na_2MnP_2O_7$ polymorph with triclinic (*P*1) symmetry are listed.

a (Å) = 9.92230	α (°) = 148.3870	space group = *P*1
b (Å) = 11.08390	β (°) = 121.9450	Rp = 8.48 %, Rwp = 12.34 %
c (Å) = 12.47260	γ (°) = 68.4230	χ^2 = 9.08 %

Atom	Wyckoff	x	y	z	Occupancy	B (iso)	Symmetry
Mn1	*1a*	0.49320	0.42940	0.15810	1.000	1.000	1
Mn2	*1a*	0.90020	0.86270	0.64380	1.000	1.000	1
Mn3	*1a*	0.49890	0.60150	0.86500	1.000	1.000	1
Mn4	*1a*	0.11150	0.19060	0.40020	1.000	1.000	1
P1	*1a*	0.17400	0.33800	0.12100	1.000	1.000	1
P2	*1a*	0.70600	0.73100	0.27000	1.000	1.000	1
P3	*1a*	0.19300	0.53100	0.49000	1.000	1.000	1
P4	*1a*	0.44900	0.00400	0.31600	1.000	1.000	1
P5	*1a*	0.83800	0.68900	0.90700	1.000	1.000	1
P6	*1a*	0.28940	0.25100	0.70100	1.000	1.000	1
P7	*1a*	0.80000	0.46600	0.50500	1.000	1.000	1
P8	*1a*	0.54600	-0.01900	0.66200	1.000	1.000	1
Na1	*1a*	0.84700	0.11600	0.45400	1.000	1.000	1
Na2	*1a*	0.14200	0.91200	0.57800	1.000	1.000	1
Na3	*1a*	0.85500	0.14100	0.04900	1.000	1.000	1
Na4	*1a*	0.15400	0.78400	0.92600	1.000	1.000	1
Na5	*1a*	0.17400	0.68300	0.14900	1.000	1.000	1
Na6	*1a*	0.81400	0.33300	0.85700	1.000	1.000	1
Na7	*1a*	0.53400	-0.00700	-0.02000	1.000	1.000	1
Na8	*1a*	0.48300	0.27200	0.31700	1.000	1.000	1
O1	*1a*	0.26500	0.44100	0.34500	1.000	1.000	1
O2	*1a*	0.32100	0.64100	0.70300	1.000	1.000	1
O3	*1a*	0.08600	0.29400	0.30200	1.000	1.000	1
O4	*1a*	0.09600	0.72200	0.57300	1.000	1.000	1
O5	*1a*	0.30000	0.19500	0.01600	1.000	1.000	1
O6	*1a*	0.06500	0.48800	0.13000	1.000	1.000	1
O7	*1a*	0.03000	0.15700	-0.03600	1.000	1.000	1
O8	*1a*	0.53600	0.81900	0.27700	1.000	1.000	1
O9	*1a*	0.72900	0.57000	0.25400	1.000	1.000	1
O10	*1a*	0.85400	0.95300	0.50200	1.000	1.000	1
O11	*1a*	0.68000	0.60000	0.05000	1.000	1.000	1
O12	*1a*	0.48200	0.97100	0.18400	1.000	1.000	1
O13	*1a*	0.27000	0.94900	0.23800	1.000	1.000	1
O14	*1a*	0.54200	0.26200	0.56000	1.000	1.000	1
O15	*1a*	0.74200	0.55900	0.66500	1.000	1.000	1
O16	*1a*	0.66800	0.36300	0.30400	1.000	1.000	1
O17	*1a*	0.92300	0.31500	0.49100	1.000	1.000	1
O18	*1a*	0.88400	0.67000	0.62400	1.000	1.000	1
O19	*1a*	0.71100	0.78100	0.99900	1.000	1.000	1
O20	*1a*	0.87500	0.47200	0.82000	1.000	1.000	1
O21	*1a*	0.93600	0.91300	0.05700	1.000	1.000	1
O22	*1a*	0.45600	0.14900	0.68100	1.000	1.000	1
O23	*1a*	0.14900	0.02200	0.46200	1.000	1.000	1
O24	*1a*	0.26300	0.37300	0.88600	1.000	1.000	1
O25	*1a*	0.31000	0.42400	0.74900	1.000	1.000	1
O26	*1a*	0.72500	0.05700	0.75900	1.000	1.000	1
O27	*1a*	0.51800	0.06900	0.82900	1.000	1.000	1
O28	*1a*	0.43900	0.73700	0.42600	1.000	1.000	1

Table S2. Selected bond lengths and bond valence sum (BVS) values of β-$Na_2MnP_2O_7$.

Mn1-O5:	2.4065Å	s=0.1980v.u.	Mn2-O4:	2.0562Å	s=0.4102v.u.
Mn1-O9:	2.4246Å	s=0.1907v.u.	Mn2-O7:	1.9255Å	s=0.5383v.u.
Mn1-O16:	2.2054Å	s=0.3008v.u.	Mn2-O9:	2.3446Å	s=0.2252v.u.
Mn1-O24:	2.5218Å	s=0.1558v.u.	Mn2-O10:	2.4818Å	s=0.1693v.u.
Mn1-O27:	2.2989Å	s=0.2477v.u.	Mn2-O18:	1.9902Å	s=0.4705v.u.
Mn1-O28:	2.0562Å	s=0.4102v.u.	Mn2-O26:	2.0842Å	s=0.3870v.u.
BV-sum of Mn1: 1.6344v.u.			**BV-sum of Mn2: 2.3183v.u.**		

Mn3-O2:	2.1341Å	s=0.3489v.u.	Mn4-O3:	2.1742Å	s=0.3209v.u.
Mn3-O8:	3.1472Å	s=0.0425v.u.	Mn4-O13:	2.1861Å	s=0.3131v.u.
Mn3-O11:	2.0516Å	s=0.4141v.u.	Mn4-O17:	2.0898Å	s=0.3826v.u.
Mn3-O12:	2.2536Å	s=0.2721v.u.	Mn4-O21:	2.1078Å	s=0.3684v.u.
Mn3-O14:	2.2296Å	s=0.2861v.u.	Mn4-O23:	2.4215Å	s=0.1920v.u.
Mn3-O19:	2.2079Å	s=0.2993v.u.	Mn4-O25:	2.2382Å	s=0.2810v.u.
Mn3-O25:	2.1146Å	s=0.3633v.u.			
BV-sum of Mn3: 2.1301v.u.			**BV-sum of Mn4: 1.9931v.u.**		

P1-O1:	1.6064Å	s=1.0326v.u.	P2-O8:	1.6140Å	s=1.0147v.u.
P1-O5:	1.5906Å	s=1.0706v.u.	P2-O9:	1.5552Å	s=1.1609v.u.
P1-O6:	1.5603Å	s=1.1474v.u.	P2-O10:	1.6180Å	s=1.0054v.u.
P1-O7:	1.5353Å	s=1.2149v.u.	P2-O11:	1.5635Å	s=1.1389v.u.
BV-sum of P1: 4.5802v.u.			**BV-sum of P2: 4.4312v.u.**		

P3-O1:	1.5958Å	s=1.0579v.u.	P4-O8:	1.6217Å	s=0.9970v.u.
P3-O2:	1.4863Å	s=1.3592v.u.	P4-O12:	1.5519Å	s=1.1697v.u.
P3-O3:	1.5657Å	s=1.1332v.u.	P4-O13:	1.5590Å	s=1.1509v.u.
P3-O4:	1.5175Å	s=1.2654v.u.	P4-O14:	1.5611Å	s=1.1452v.u.
BV-sum of P3: 4.9170v.u.			**BV-sum of P4: 4.5800v.u.**		

P5-O15:	1.6289Å	s=0.9806v.u.	P6-O22:	1.6293Å	s=0.9798v.u.
P5-O19:	1.5927Å	s=1.0655v.u.	P6-O23:	1.6089Å	s=1.0267v.u.
P5-O20:	1.5570Å	s=1.1561v.u.	P6-O24:	1.5119Å	s=1.2816v.u.
P5-O21:	1.5966Å	s=1.0559v.u.	P6-O25:	1.5102Å	s=1.2868v.u.
BV-sum of P5: 4.3648v.u.			**BV-sum of P6: 4.7061v.u.**		

P7-O15:	1.6283Å	s=0.9819v.u.	P8-O22:	1.6032Å	s=1.0401v.u.
P7-O16:	1.4332Å	s=1.5347v.u.	P8-O26:	1.5551Å	s=1.1611v.u.
P7-O17:	1.5958Å	s=1.0579v.u.	P8-O27:	1.5231Å	s=1.2494v.u.
P7-O18:	1.5399Å	s=1.2023v.u.	P8-O28:	1.5335Å	s=1.2199v.u.

BV-sum of P7: 4.8675v.u. **BV-sum of P8: 4.7711v.u.**

Na1-O10:	2.3094Å	s=0.2122v.u.	Na2-O4:	2.2584Å	s=0.2359v.u.
Na1-O12:	3.0326Å	s=0.0473v.u.	Na2-O5:	2.7402Å	s=0.0868v.u.
Na1-O15:	3.0415Å	s=0.0465v.u.	Na2-O6:	2.6999Å	s=0.0944v.u.
Na1-O17:	2.1836Å	s=0.2755v.u.	Na2-O10:	2.4866Å	s=0.1469v.u.
Na1-O19:	2.7396Å	s=0.0869v.u.	Na2-O23:	2.5995Å	s=0.1162v.u.
Na1-O20:	2.2958Å	s=0.2183v.u.	Na2-O24:	2.9166Å	s=0.0602v.u.
Na1-O23:	2.7639Å	s=0.0827v.u.			

BV-sum of Na1: 1.1092v.u. **BV-sum of Na2: 0.9033v.u.**

Na3-O3:	2.0439Å	s=0.3681v.u.	Na4-O2:	2.9036Å	s=0.0619v.u.
Na3-O7:	2.5817Å	s=0.1206v.u.	Na4-O12:	2.7860Å	s=0.0790v.u.
Na3-O9:	3.0022Å	s=0.0504v.u.	Na4-O13:	2.1213Å	s=0.3135v.u.
Na3-O16:	3.0283Å	s=0.0478v.u.	Na4-O17:	3.0462Å	s=0.0460v.u.
Na3-O18:	2.9684Å	s=0.0541v.u.	Na4-O18:	2.5821Å	s=0.1205v.u.
Na3-O21:	2.4275Å	s=0.1661v.u.	Na4-O21:	2.6228Å	s=0.1108v.u.
Na3-O26:	2.4133Å	s=0.1711v.u.	Na4-O25:	2.6946Å	s=0.0954v.u.
Na3-O27:	2.8055Å	s=0.0758v.u.			

BV-sum of Na3: 1.1466v.u. **BV-sum of Na4: 0.9654v.u.**

Na5-O6:	2.5442Å	s=0.1304v.u.	Na6-O6:	2.2266Å	s=0.2520v.u.
Na5-O13:	2.4909Å	s=0.1456v.u.	Na6-O7:	2.9176Å	s=0.0601v.u.
Na5-O20:	2.6429Å	s=0.1062v.u.	Na6-O10:	2.5237Å	s=0.1360v.u.
Na5-O23:	2.1854Å	s=0.2745v.u.	Na6-O11:	2.1633Å	s=0.2874v.u.
Na5-O24:	2.2322Å	s=0.2491v.u.	Na6-O14:	2.7646Å	s=0.0825v.u.
Na5-O28:	2.6890Å	s=0.0965v.u.	Na6-O20:	2.2683Å	s=0.2311v.u.
			Na6-O26:	2.4715Å	s=0.1516v.u.

BV-sum of Na5: 1.1306v.u. **BV-sum of Na6: 1.3179v.u.**

Na7-O2:	2.6466Å	s=0.1054v.u.	Na8-O1:	2.2394Å	s=0.2454v.u.
Na7-O5:	2.4846Å	s=0.1476v.u.	Na8-O5:	2.5668Å	s=0.1244v.u.
Na7-O12:	3.0558Å	s=0.0451v.u.	Na8-O12:	2.1126Å	s=0.3192v.u.
Na7-O16:	2.2393Å	s=0.2455v.u.	Na8-O14:	2.8615Å	s=0.0675v.u.
Na7-O19:	2.4769Å	s=0.1499v.u.	Na8-O15:	2.5011Å	s=0.1426v.u.
Na7-O27:	2.5631Å	s=0.1254v.u.	Na8-O16:	2.5235Å	s=0.1361v.u.

BV-sum of Na7: 0.9157v.u. **BV-sum of Na8: 1.1513v.u.**

P1-O1:	1.6064Å	s=1.0326v.u.	Mn3-O2:	2.1340Å	s=0.3489v.u.
P3-O1:	1.5958Å	s=1.0579v.u.	P3-O2:	1.4862Å	s=1.3593v.u.
Na8-O1:	2.2394Å	s=0.2454v.u.	Na4-O2:	2.9036Å	s=0.0619v.u.
			Na7-O2:	2.6466Å	s=0.1054v.u.

BV-sum of O1: 2.4309v.u.

BV-sum of O2: 1.9702v.u.

Mn4-O3:	2.1742Å	s=0.3209v.u.	Mn2-O4:	2.0561Å	s=0.4103v.u.
P3-O3:	1.5658Å	s=1.1331v.u.	P3-O4:	1.5176Å	s=1.2653v.u.
Na3-O3:	2.0439Å	s=0.3681v.u.	Na2-O4:	2.2584Å	s=0.2359v.u.

BV-sum of O3: 1.9483v.u.

BV-sum of O4: 2.0090v.u.

Mn1-O5:	2.4065Å	s=0.1980v.u.	P1-O6:	1.5603Å	s=1.1473v.u.
P1-O5:	1.5906Å	s=1.0706v.u.	Na2-O6:	2.6999Å	s=0.0944v.u.
Na2-O5:	2.7402Å	s=0.0868v.u.	Na5-O6:	2.5443Å	s=0.1304v.u.
Na7-O5:	2.4845Å	s=0.1476v.u.	Na6-O6:	2.2267Å	s=0.2520v.u.
Na8-O5:	2.5669Å	s=0.1244v.u.			

BV-sum of O5: 1.6786v.u.

BV-sum of O6: 1.6889v.u.

Mn2-O7:	1.9255Å	s=0.5383v.u.	Mn3-O8:	3.1472Å	s=0.0425v.u.
P1-O7:	1.5354Å	s=1.2148v.u.	P2-O8:	1.6140Å	s=1.0147v.u.
Na3-O7:	2.5817Å	s=0.1206v.u.	P4-O8:	1.6217Å	s=0.9969v.u.
Na6-O7:	2.9176Å	s=0.0601v.u.			

BV-sum of O7: 2.0190v.u.

BV-sum of O8: 2.2008v.u.

Mn1-O9:	2.4246Å	s=0.1907v.u.	Mn2-O10:	2.4818Å	s=0.1693v.u.
Mn2-O9:	2.3446Å	s=0.2252v.u.	P2-O10:	1.6181Å	s=1.0053v.u.
P2-O9:	1.5551Å	s=1.1610v.u.	Na1-O10:	2.3094Å	s=0.2122v.u.
Na3-O9:	3.0022Å	s=0.0504v.u.	Na2-O10:	2.4866Å	s=0.1469v.u.
			Na6-O10:	2.5238Å	s=0.1360v.u.

BV-sum of O9: 1.6999v.u.

BV-sum of O10: 1.7067v.u.

Mn3-O11:	2.0516Å	s=0.4141v.u.	Mn3-O12:	2.2536Å	s=0.2721v.u.
P2-O11:	1.5635Å	s=1.1389v.u.	P4-O12:	1.5518Å	s=1.1699v.u.
Na6-O11:	2.1633Å	s=0.2874v.u.	Na1-O12:	3.0325Å	s=0.0473v.u.
			Na4-O12:	2.7860Å	s=0.0790v.u.
			Na7-O12:	3.0559Å	s=0.0451v.u.
			Na8-O12:	2.1126Å	s=0.3192v.u.

BV-sum of O11: 1.9398v.u.

BV-sum of O12: 1.9700v.u.

Mn4-O13:	2.1861Å	s=0.3131v.u.	Mn3-O14:	2.2296Å	s=0.2861v.u.
P4-O13:	1.5590Å	s=1.1508v.u.	P4-O14:	1.5612Å	s=1.1451v.u.
Na4-O13:	2.1213Å	s=0.3136v.u.	Na6-O14:	2.7646Å	s=0.0825v.u.
Na5-O13:	2.4908Å	s=0.1457v.u.	Na8-O14:	2.8614Å	s=0.0675v.u.

BV-sum of O13: 1.9885v.u. **BV-sum of O14: 1.6837v.u.**

P5-O15:	1.6289Å	s=0.9806v.u.	Mn1-O16:	2.2054Å	s=0.3008v.u.
P7-O15:	1.6284Å	s=0.9818v.u.	P7-O16:	1.4332Å	s=1.5346v.u.
Na1-O15:	3.0415Å	s=0.0465v.u.	Na3-O16:	3.0283Å	s=0.0478v.u.
Na8-O15:	2.5010Å	s=0.1426v.u.	Na7-O16:	2.2393Å	s=0.2454v.u.
			Na8-O16:	2.5236Å	s=0.1361v.u.

BV-sum of O15: 2.2369v.u. **BV-sum of O16: 2.3158v.u.**

Mn4-O17:	2.0898Å	s=0.3826v.u.	Mn2-O18:	1.9902Å	s=0.4705v.u.
P7-O17:	1.5958Å	s=1.0579v.u.	P7-O18:	1.5399Å	s=1.2023v.u.
Na1-O17:	2.1836Å	s=0.2755v.u.	Na3-O18:	2.9685Å	s=0.0541v.u.
Na4-O17:	3.0462Å	s=0.0460v.u.	Na4-O18:	2.5820Å	s=0.1206v.u.

BV-sum of O17: 1.8667v.u. **BV-sum of O18: 1.9387v.u.**

Mn3-O19:	2.2079Å	s=0.2993v.u.	P5-O20:	1.5569Å	s=1.1562v.u.
P5-O19:	1.5927Å	s=1.0654v.u.	Na1-O20:	2.2958Å	s=0.2183v.u.
Na1-O19:	2.7396Å	s=0.0869v.u.	Na5-O20:	2.6429Å	s=0.1062v.u.
Na7-O19:	2.4769Å	s=0.1499v.u.	Na6-O20:	2.2683Å	s=0.2311v.u.

BV-sum of O19: 1.6785v.u. **BV-sum of O20: 1.7768v.u.**

Mn4-O21:	2.1078Å	s=0.3685v.u.	P6-O22:	1.6292Å	s=0.9799v.u.
P5-O21:	1.5966Å	s=1.0560v.u.	P8-O22:	1.6032Å	s=1.0401v.u.
Na3-O21:	2.4276Å	s=0.1661v.u.			
Na4-O21:	2.6228Å	s=0.1108v.u.			

BV-sum of O21: 1.7968v.u. **BV-sum of O22: 2.1940v.u.**

Mn4-O23:	2.4214Å	s=0.1920v.u.	Mn1-O24:	2.5218Å	s=0.1558v.u.
P6-O23:	1.6089Å	s=1.0266v.u.	P6-O24:	1.5120Å	s=1.2816v.u.
Na1-O23:	2.7639Å	s=0.0827v.u.	Na2-O24:	2.9166Å	s=0.0602v.u.
Na2-O23:	2.5995Å	s=0.1162v.u.	Na5-O24:	2.2322Å	s=0.2491v.u.
Na5-O23:	2.1853Å	s=0.2745v.u.			

BV-sum of O23: 1.7337v.u. **BV-sum of O24: 1.8171v.u.**

Mn3-O25:	2.1146Å	s=0.3633v.u.	Mn2-O26:	2.0842Å	s=0.3870v.u.
Mn4-O25:	2.2382Å	s=0.2810v.u.	P8-O26:	1.5551Å	s=1.1610v.u.
P6-O25:	1.5102Å	s=1.2869v.u.	Na3-O26:	2.4133Å	s=0.1711v.u.
Na4-O25:	2.6947Å	s=0.0954v.u.	Na6-O26:	2.4715Å	s=0.1516v.u.

BV-sum of O25: 2.0984v.u. **BV-sum of O26: 1.9294v.u.**

Mn1-O27:	2.2989Å	s=0.2477v.u.	Mn1-O28:	2.0562Å	s=0.4102v.u.
P8-O27:	1.5231Å	s=1.2493v.u.	P8-O28:	1.5336Å	s=1.2198v.u.
Na3-O27:	2.8055Å	s=0.0758v.u.	Na5-O28:	2.6890Å	s=0.0966v.u.
Na7-O27:	2.5631Å	s=0.1254v.u.			

BV-sum of O27: 1.7883v.u. **BV-sum of O28: 1.8328v.u.**

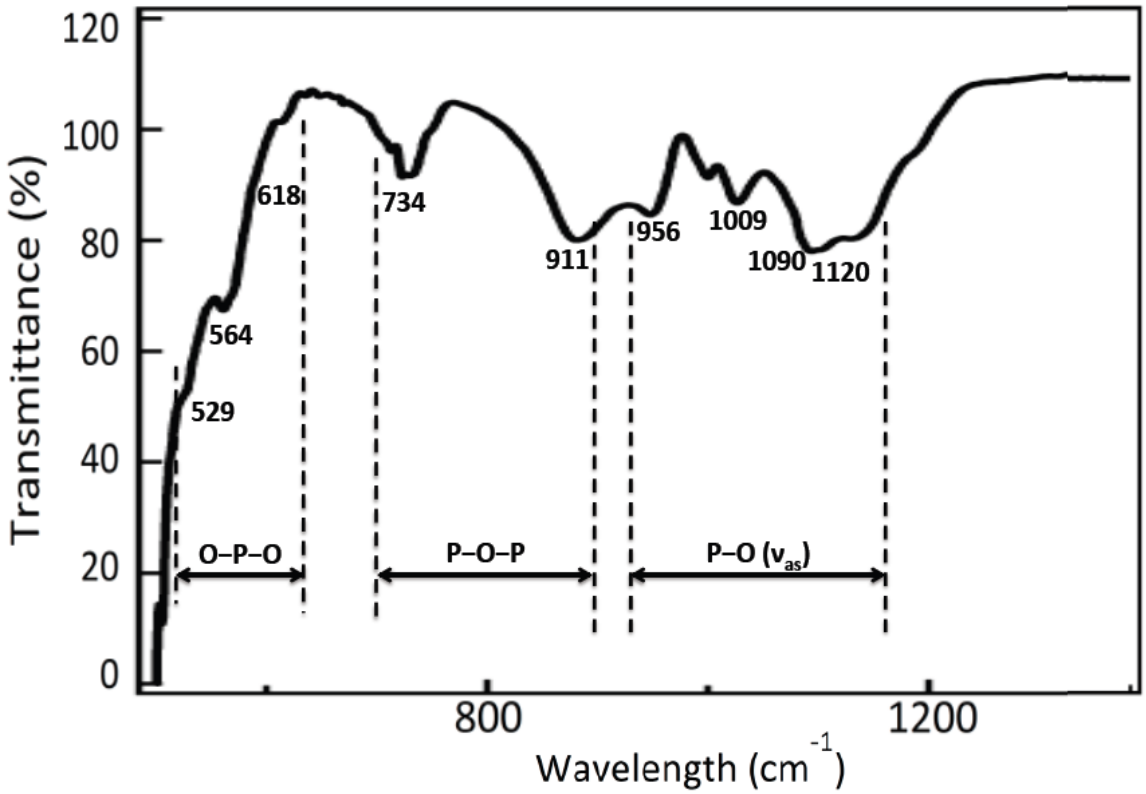

Figure S1. FT-IR spectrum of β-$Na_2MnP_2O_7$ polymorph, showing the classical P-O-P, O-P-O and P-O bands arising from the characteristics diphosphate (P_2O_7) groups.

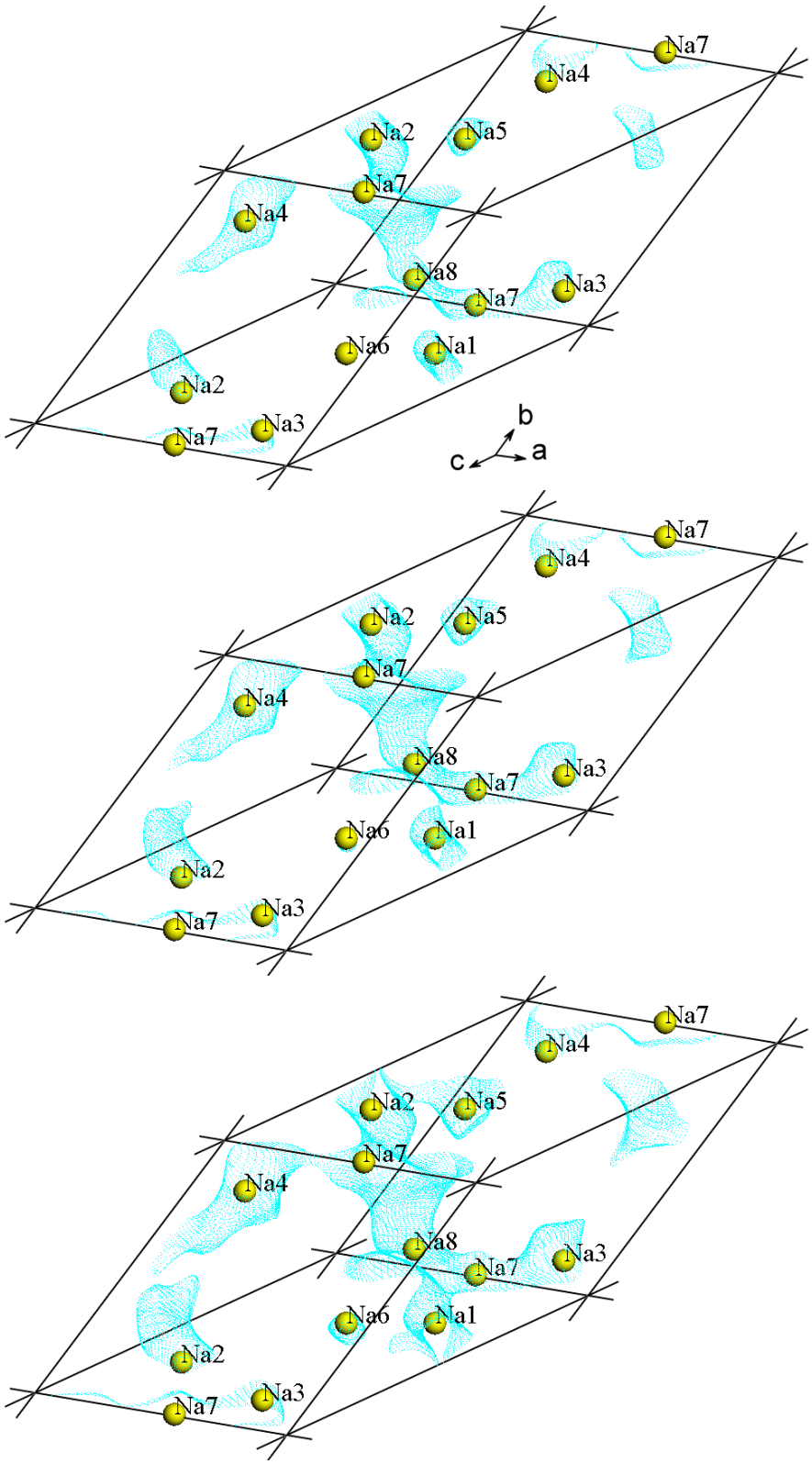

Figure S2. Bond-valence mismatch maps with isovalues 0.25, 0.35, and 0.45 from top to bottom, respectively. The most suitable Na^+ diffusion pathways connect Na7-Na8-Na7 sites.

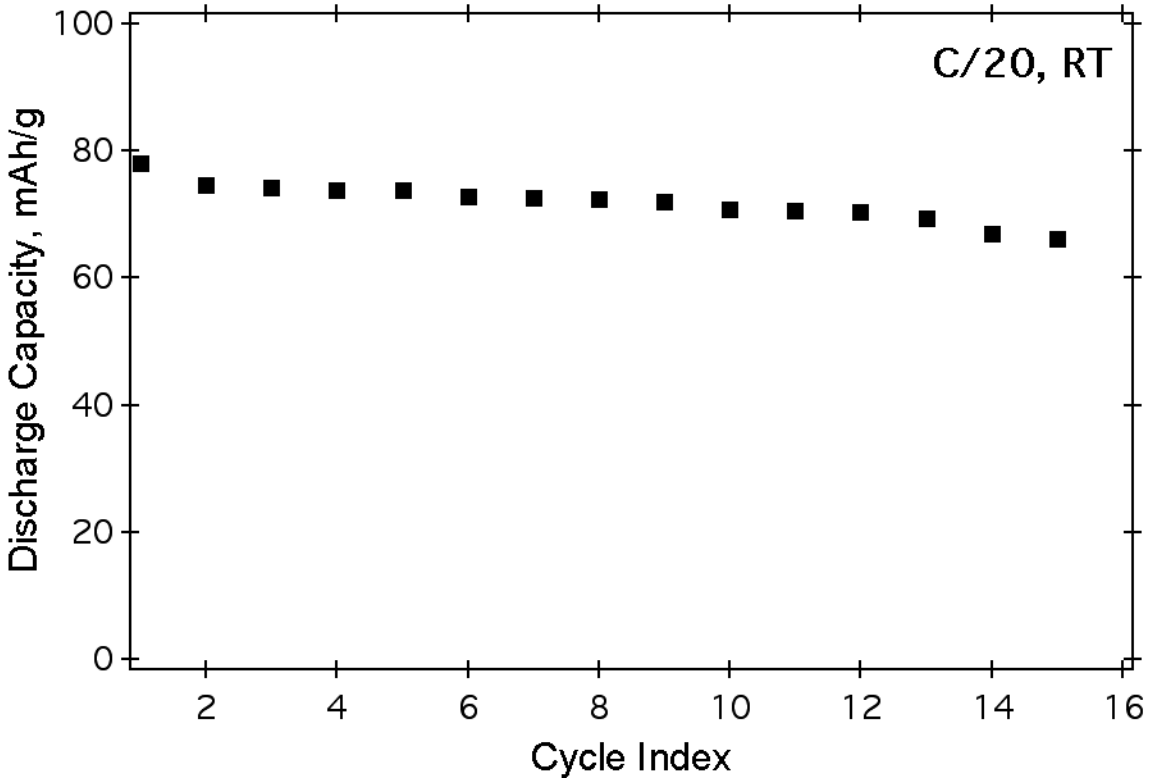

Figure S3. Initial cycling stability of $Na_2MnP_2O_7$ cathode (at a rate of C/20 at 25 °C) shown for the first 15 cycles.