Electronic Supplementary Information

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Title Defect Chemistry and Lithium-Ion Migration in Polymorphs of the Cathode Material Li_2MnSiO_4

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Table S1. (a) Pair potential parameters, (b) shell parameters, and (c) three-body parameters used in the simulation of Li_2MnSiO_4.

(a)

Interaction	A (eV)	ρ (Å)	C (eV.Å^6)
Li^+ - O^{2-}	632.1018	0.2906	0
Mn^{2+} - O^{2-}	2601.394	0.2780	0
Si^{4+} - O^{2-}	1283.91	0.32052	10.66
O^{2-} - O^{2-}	22764.3	0.149	27.89

(b)

Species	Y (e)	k (eV.Å^{-2})
Mn^{2+}	3.42	95.00
O^{2-}	-2.86	74.92

(c)

Bonds	K (eV. rad^{-2})	θ_0 (^{o})
O^{2-} - Si^{4+} - O^{2-}	2.09724	109.4

Table S2. Selected bond length and angle ranges for four polymorphs of Li_2MnSiO_4.

Experimental values are given in parentheses.

	Bond			
Phase	Li1-O (Å)	Li2-O (Å)	Mn-O (Å)	Si-O (Å)
Pmn2₁	1.95~2.02	N/A	2.06~2.10	1.63~1.64
	(1.88~2.21)		(2.02~2.07)	(1.65~1.71)
Pmnb	1.94~2.01	N/A	2.05~2.10	1.63~1.64
	(1.93~2.03)		(2.03~2.21)	(1.62~1.69)
P2₁/n	1.95~2.07	1.93~2.28	2.03~2.09	1.63~1.64
	(1.90~2.04)	(1.92~2.14)	(2.01~2.09)	(1.65~1.66)
Pn	1.97~2.15	1.92~2.16	2.03-2.08	1.63~1.64
	(N/A)	(N/A)	(N/A)	(N/A)
	Angle			
Phase	O-Li1-O (°)	O-Li2-O (°)	O-Mn-O (°)	O-Si-O (°)
Pmn2₁	107.2~113.5	N/A	100.6~130.0	106.4~111.6
	(100.3~121.2)		(105.7~122.7)	(104.5~113.3)
Pmnb	95.8~117.8	N/A	102.3~129.2	107.2~112.0
	(96.0~119.6)		(103.5~126.0)	(104.5~125.7)
P2₁/n	95.9~117.3	87.8~124.9	93.3~119.3	106.5~110.7
	(95.8~120.4)	(89.6~127.6)	(92.8~118.3)	(107.5~111.7)
Pn	104.2~122.1	102.6~112.8	103.2~118.1	106.1~112.3
	(N/A)	(N/A)	(N/A)	(N/A)