SUPPORTING INFORMATION

Charge Localization and Transport in Lithiated Olivine Phosphate Materials

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Table S1. Custom local Gaussian orbital basis set exponents ($bohr^{-2}$) and coefficients developed and used for the Li, P, O and transitions metals (Mn, Fe and Ni) in the Crystal06 calculations.

Atom	Shell type	Exponents	Coefficient	
			s	p, d
Li	1s	840.0	0.00268	
		217.5	0.00831	
		72.3	0.03515	
		19.65984	0.19037	
		5.0453	0.64271	
		1.50112	0.99815	
	2sp	0.50994	1.0	1.0
P	1s	202703.0	0.00012	
		22413.10	0.00128	
		4625.10	0.00697	
		1312.0	0.02744	
		425.1	0.09647	
		146.0	0.26676	
		51.8	0.47538	
		19.0	0.30123	
	2sp	339.40	0.00091	0.00286
		94.9	-0.03649	0.02859
		23.10	-0.14998	0.17429

		6.97987	0.35374	0.4212
		2.26994	0.91109	0.41142
	3sp	1.20	-0.37219	0.09071
		0.47912	1.26995	0.93503
	4sp	0.135	1.0	1.0
	3d	0.74429		1.0
O	1s	8020.0	0.00108	
		1338.0	0.00804	
		255.4	0.05324	
		69.22	0.1681	
		23.90	0.3581	
		9.264	0.3855	
		3.851	0.1468	
		1.212	0.0728	
	2sp	49.43	-0.00883	0.00958
		10.47	-0.0915	0.0696
		3.235	-0.0402	0.2065
		1.217	0.379	0.347
	3sp	0.50	1.0	1.0
	4sp	0.191	1.0	1.0
Mn	3sp	25.10023	0.00283	-0.08020
		6.05152	1.64992	-1.12946
		5.01472	1.38311	1.32955

		2.46856	-2.06227	1.00546
	4sp	1.25676	1.0	1.0
	5sp	0.51568	1.0	1.0
	3d	38.39402		0.03028
		10.50328		0.17168
		3.53013		0.44988
	4d	1.16766		1.0
	5d	0.33248		1.0
Fe	3sp	25.10082	0.03157	-0.09062
		6.03032	1.64906	-1.06639
		5.05356	1.37962	1.3494
		2.48883	-2.06518	1.00854
	4sp	1.3326	1.0	1.0
	5sp	0.5088	1.0	1.0
	3d	38.39394		0.0340
		10.50448		0.18599
		3.52198		0.4433
	4d	1.15737		1.0
	5d	0.30254		1.0
Ni	3sp	25.05574	0.00988	-0.20349
		7.14735	1.73624	-1.16436
		5.46636	0.97587	1.90865
		3.45893	-2.31627	0.84717

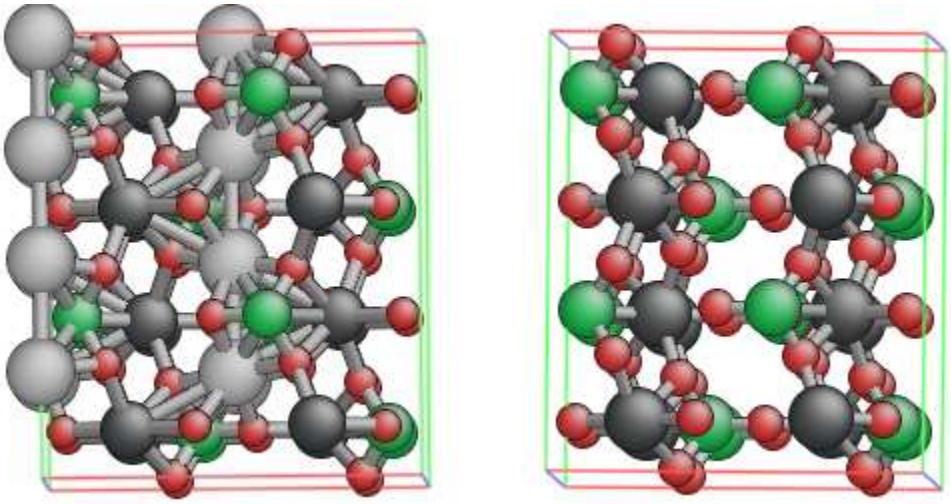
4sp	1.85958	1.0	1.0
5sp	0.807145	1.0	1.0
3d	45.36535		0.21568
	12.69085		1.12511
	4.37552		2.54918
4d	1.48636		1.0
5d	0.43093		1.0

Table S2. Optimized lattice parameters and fractional coordinates of transition metal and four sets of oxygen sites using VASP.

Compounds	Lattice Constant [a, b, c] (Å)	TM	O
$LiMnPO_4$	[10.6007, 6.1761, 4.7887]	(0.2799, 1/4, 0.9584)	(0.9593, 1/4, 0.7483) (0.4544, 1/4, 0.2069) (0.1587, 0.0458, 0.2901) (0.3413, 0.5458, 0.7901)
$MnPO_4$	[9.8561, 6.0363, 4.7906]	(0.2965, 1/4, 0.9928)	(0.1394, 1/4, 0.7438) (0.4589, 1/4, 0.1057) (0.1730, 0.0499, 0.2819) (0.3269, 0.5499, 0.7819)
$LiFePO_4$	[10.3878, 6.0702, 4.7572]	(0.2799, 1/4, 0.9865)	(0.0954, 1/4, 0.7612) (0.4595, 1/4, 0.1946) (0.1677, 0.0452, 0.3052) (0.3323, 0.5453, 0.8053)
$FePO_4$	[9.9612, 5.9056, 4.8501]	(0.2724, 1/4, 0.9701)	(0.1298, 1/4, 0.7295) (0.4503, 1/4, 0.1218) (0.1748, 0.0491, 0.2799) (0.3251, 0.5491, 0.7799)
$LiCoPO_4$	[10.3392, 5.9895, 4.7497]	(0.2760, 1/4, 0.9774)	(0.0997, 1/4, 0.7412) (0.4534, 1/4, 0.1996) (0.1645, 0.0444, 0.2804) (0.3355, 0.5444, 0.7804)
$CoPO_4$	[9.7579, 5.9793, 4.8527]	(0.2721, 1/4, 0.9659)	(0.1263, 1/4, 0.7219)

			(0.4431, 1/4, 0.1392) (0.1686, 0.0479, 0.2588) (0.3314, 0.5479, 0.7588)
$LiNiPO_4$	[10.1170, 5.5909, 4.7797]	(0.2739, 1/4, 0.9101)	(0.9581, 1/4, 0.7542) (0.4518, 1/4, 0.2047) (0.1679, 0.0423, 0.2873) (0.3321, 0.5423, 0.7874)
$NiPO_4$	[9.8731, 5.7438, 4.7709]	(0.2754, 1/4, 0.9902)	(0.0986, 1/4, 0.7601) (0.4513, 1/4, 0.1985) (0.1644, 0.0391, 0.2931) (0.3356, 0.5409, 0.7911)

Figure S1. (Colour online) *Pnma* crystal structure of (a) $LiT^{M}PO_4T$ and (b) $T^{M}PO_4$. O, red; Li, gray; transition metal T^{M}, black; and P, green.



(a) (b)