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A Critical Revelation of Lithium Ferromanganese Phosphates (LMFP) High Property in Mn-rich Cathode for Li-ion Batteries by Using Fe Equivalent to Occupy Mn Site

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Supplementary Tables

Table. S1 Lattice parameters of $Li(Mn_{1-x}Fe_x)PO_4/C$ sample

Sample	Lattice parameters(Å)			V(Å3)	c/a	Reliability fator(%)		
	a	b	c			x^2	R_{wp}	R_p
x=0	10.451	6.106	4.745	303.998	0.454	1.224	6.75%	13.63%
x=1/24	10.460	6.108	4.754	303.783	0.454	1.126	7.65%	13.27%
x=1/12	10.440	6.097	4.748	302.195	0.455	1.139	8.41%	13.74%
x=1/8	10.434	6.090	4.745	301.446	0.455	1.089	6.33%	13.28%
x=1/4	10.426	6.084	4.743	300.668	0.455	1.134	77.43%	12.96%

Tab. S2 Comparison of Li-O, P-O, Mn-O, Fe-O bond lengths and O-P-O bond angles of $Li(Mn_{1-x}Fe_x)PO_4$ systems

x	Li-O (Å)	Mn-O (Å)	P-O (Å)	Fe-O (Å)	O-P-O (º)
0	2.1904	2.2274	1.5604	/	112.9819
1/24	2.1918	2.2254	1.5611	2.2314	112.9824
1/12	2.1932	2.2266	1.5616	2.2356	112.9816
1/8	2.1949	2.2279	1.5619	2.2365	112.9811
1/4	2.1958	2.2287	1.5613	2.2341	112.9813

Tab. S3 Average net charges of each atom in $Li(Mn_{1-x}Fe_x)PO_4$

Material species	The average net charge of each atom (e)				
	Li	O	Mn	P	Fe
$LiMnPO_4$	-1.0500	0.8545	-4.2450	2.5860	/
$LiMn_{23/24}Fe_{1/24}PO_4$	-1.0511	0.8547	-4.2454	2.5864	1.3990
$LiMn_{11/12}Fe_{1/12}PO_4$	-1.0512	0.8547	-4.2460	2.5868	1.4000
$LiMn_{7/8}Fe_{1/8}PO_4$	-1.0516	0.8548	-4.2468	2.5865	1.3973
$LiMn_{3/4}Fe_{1/4}PO_4$	-1.0518	0.8551	-4.2485	2.5872	1.3873

Tab. S4 After 25 charge/discharge cycles, the fitting parameters in the equivalent circuit in the EIS impedance diagram of $Li(Mn_{1-x}Fe_x)PO_4/C$ materials

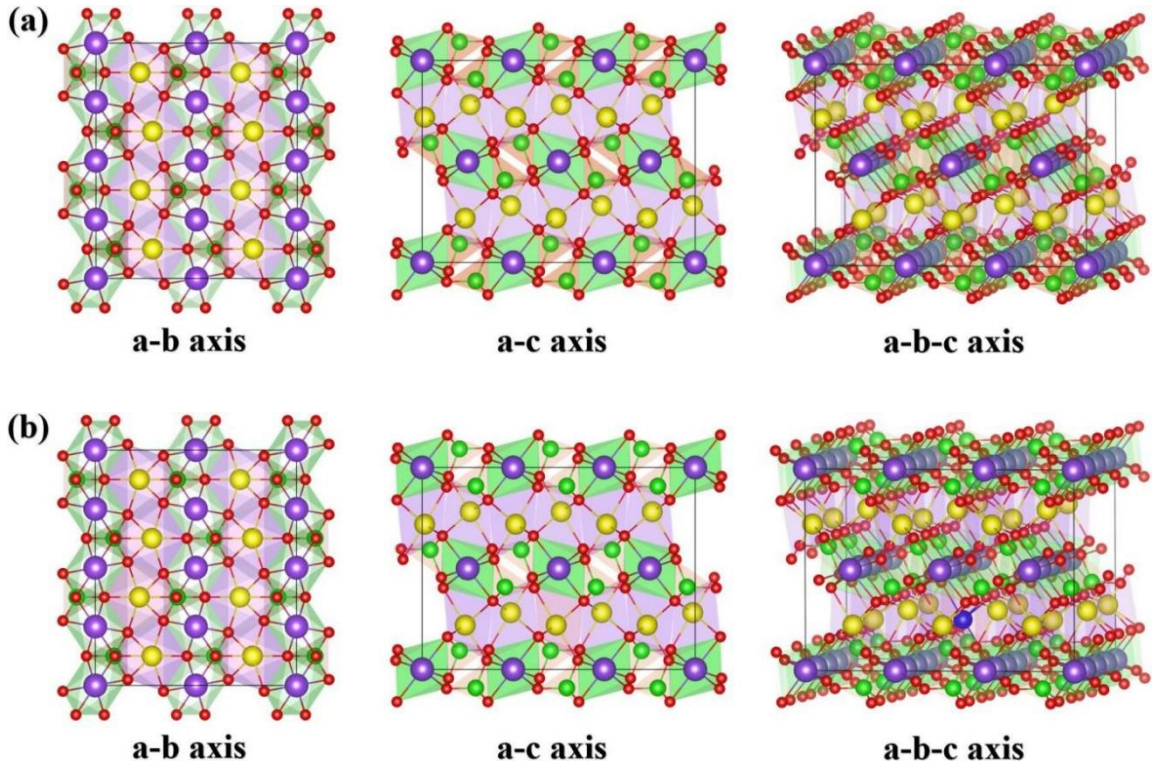
	R_e (Ω)	R_f (Ω)	CPE-T (F)	R_{ct} (Ω)

$LiMnPO_4$	7.81	12.11	2.23	106.08
$LiMn_{23/24}Fe_{1/24}PO_4$	6.58	10.51	2.95	96.91
$LiMn_{11/12}Fe_{1/12}PO_4$	4.97	8.66	4.11	80.12
$LiMn_{7/8}Fe_{1/8}PO_4$	3.33	6.02	5.03	71.24
$LiMn_{1/3}Fe_{1/4}PO_4$	2.84	5.47	6.23	55.37

Tab. S5 The D_{Li}+ and exchange current density for $Li(Mn_{1-x}Fe_x)PO_4$/C materials after 25 charge/discharge cycles

	σ ($cm^2 \cdot s^{-1/2}$)	D_{Li^+} ($cm^2 \cdot s^{-1}$)	R_{ct} (Ω)	I^0 ($mA \cdot cm^{-2}$)
$LiMnPO_4$	16.168	6.419×10^{-13}	106.08	2.42×10^{-4}
$LiMn_{23/24}Fe_{1/24}PO_4$	14.972	7.485×10^{-13}	96.91	2.65×10^{-4}
$LiMn_{11/12}Fe_{1/12}PO_4$	14.671	7.796×10^{-13}	80.12	3.20×10^{-4}
$LiMn_{7/8}Fe_{1/8}PO_4$	13.653	9.002×10^{-13}	71.24	3.60×10^{-4}
$LiMn_{1/3}Fe_{1/4}PO_4$	9.102	2.025×10^{-12}	55.37	4.64×10^{-4}

Supplementary Figures



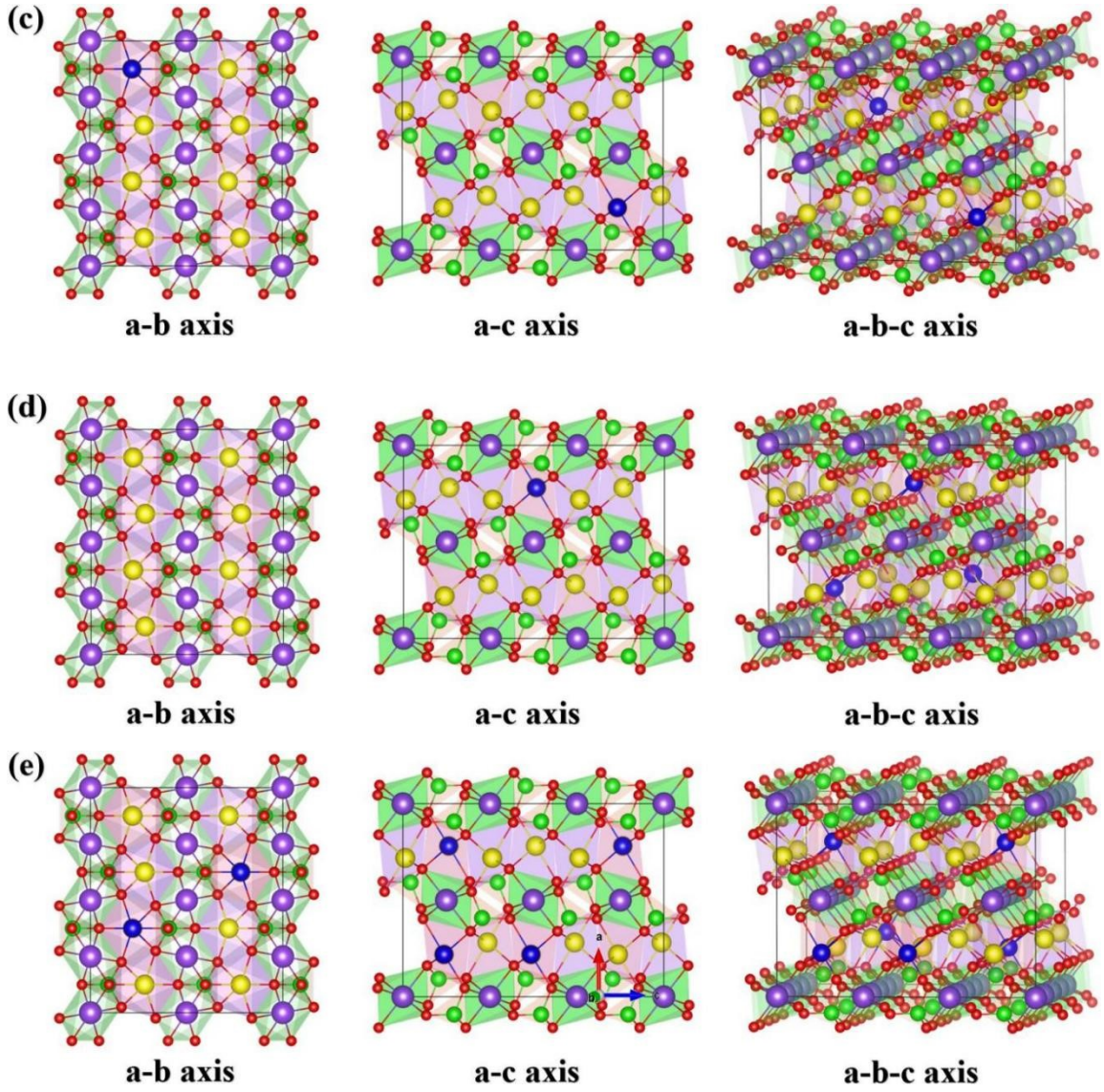
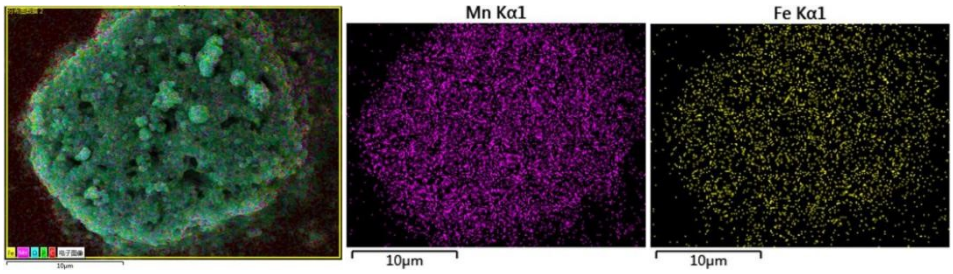


Fig. S1 Supercell structure of $Li(Mn_{1-x}Fe_x)PO_4/C$ system and position of Fe element under different doping quantities: (a) $LiMnPO_4$; (b) $LiMn_{23/24}Fe_{1/24}PO_4$; (c) $LiMn_{11/12}Fe_{1/12}PO_4$; (d) $LiMn_{7/8}Fe_{1/8}PO_4$; (e) $LiMn_{3/4}Fe_{1/4}PO_4$ (purple is Li atom, yellow is Mn atom, blue is Fe atom, green is P atom, red is O atom)



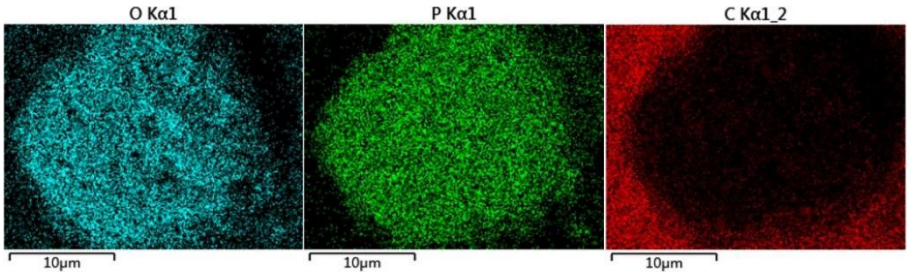


Fig. S3 The EDS pattern of $LiMn_{3/4}Fe_{1/4}PO_4/C$

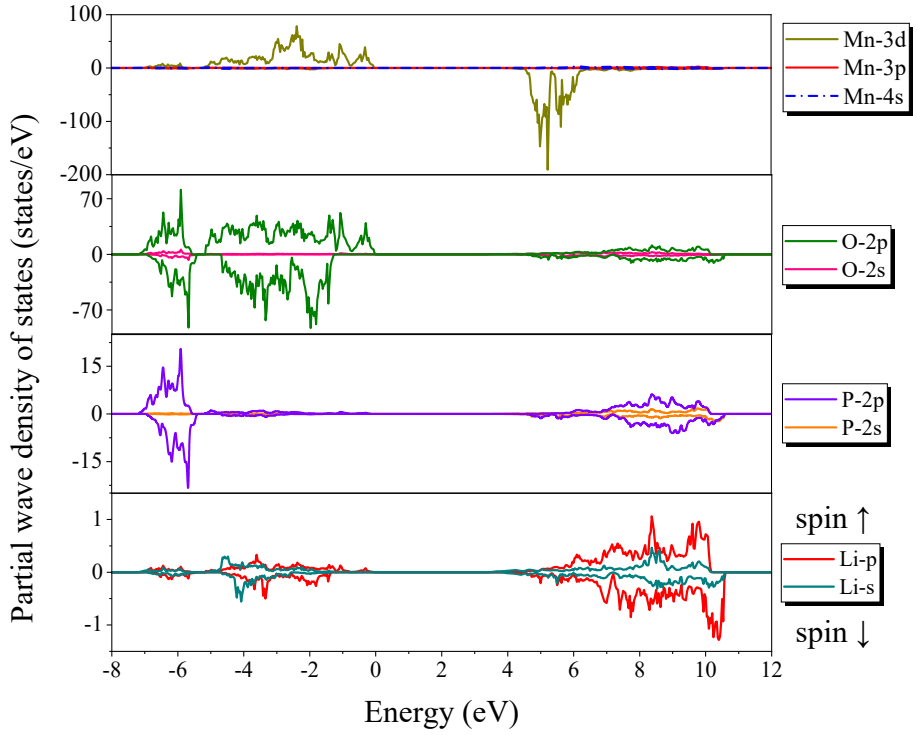


Fig. S4 Partial wave density of states (PDOS) of each atom in the s, p and d orbitals of $LiMnPO_4$ supercell

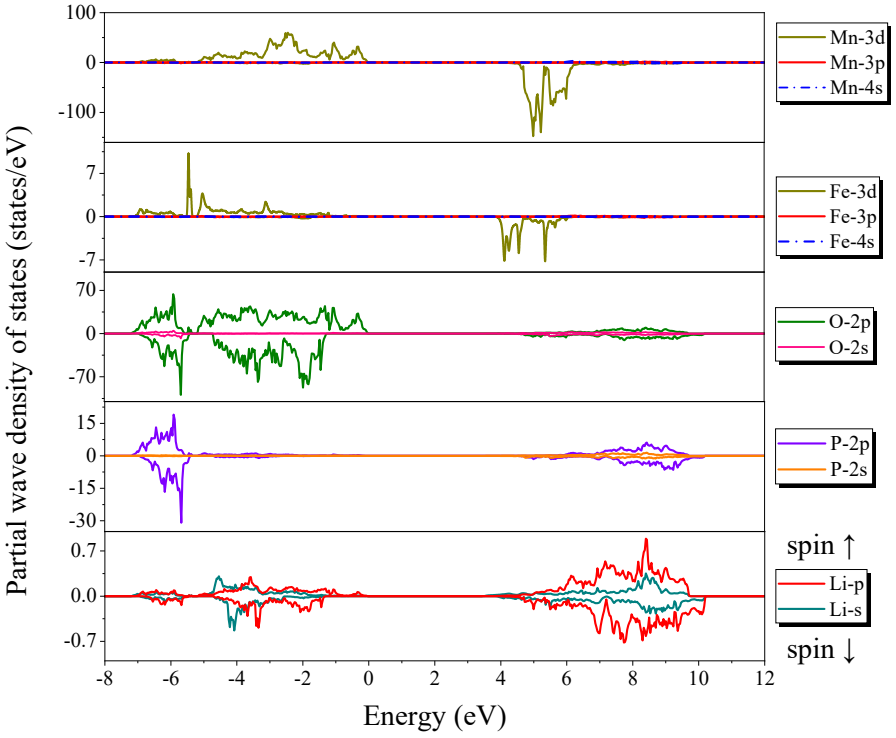


Fig. S5 Partial wave density of states (PDOS) of each atom in the s, p and d orbitals of $LiMn_{23/24}Fe_{1/24}PO_4$ supercell

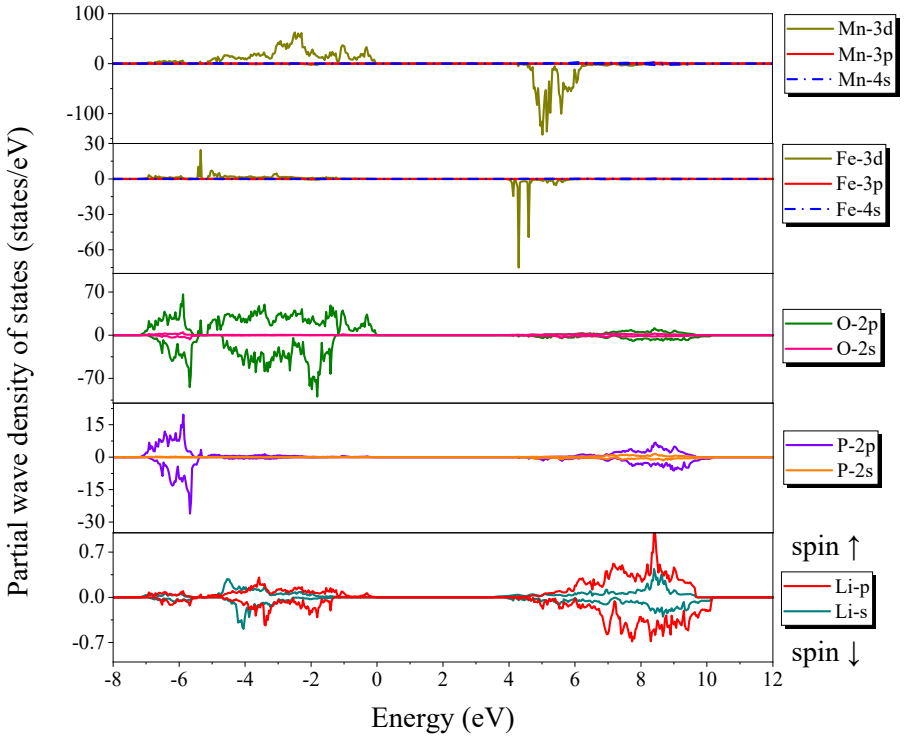


Fig. S6 Partial wave density of states (PDOS) of each atom in the s, p and d orbitals of $LiMn_{11/12}Fe_{1/12}PO_4$ supercell

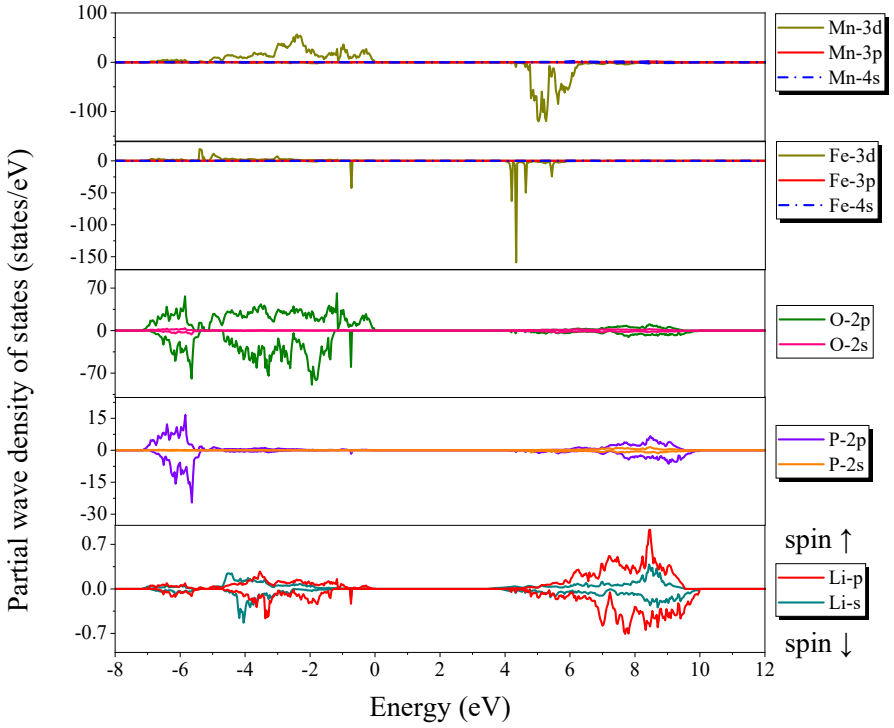


Fig. S7 Partial wave density of states (PDOS) of each atom in the s, p and d orbitals of $LiMn_{7/8}Fe_{1/8}PO_4$ supercell

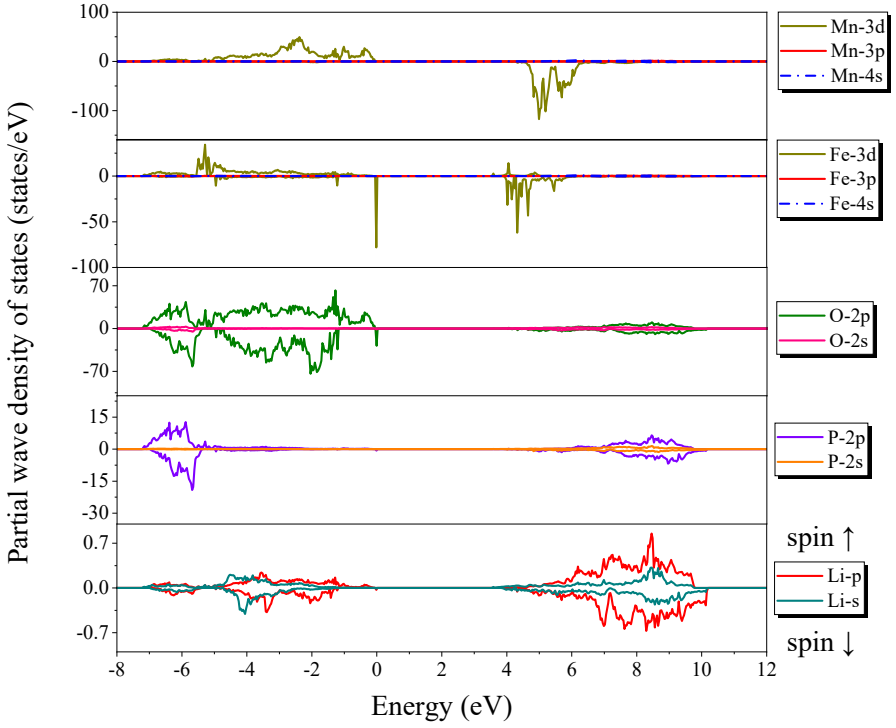


Fig. S8 Partial wave density of states (PDOS) of each atom in the s, p and d orbitals of $LiMn_{3/4}Fe_{1/4}PO_4$ supercell

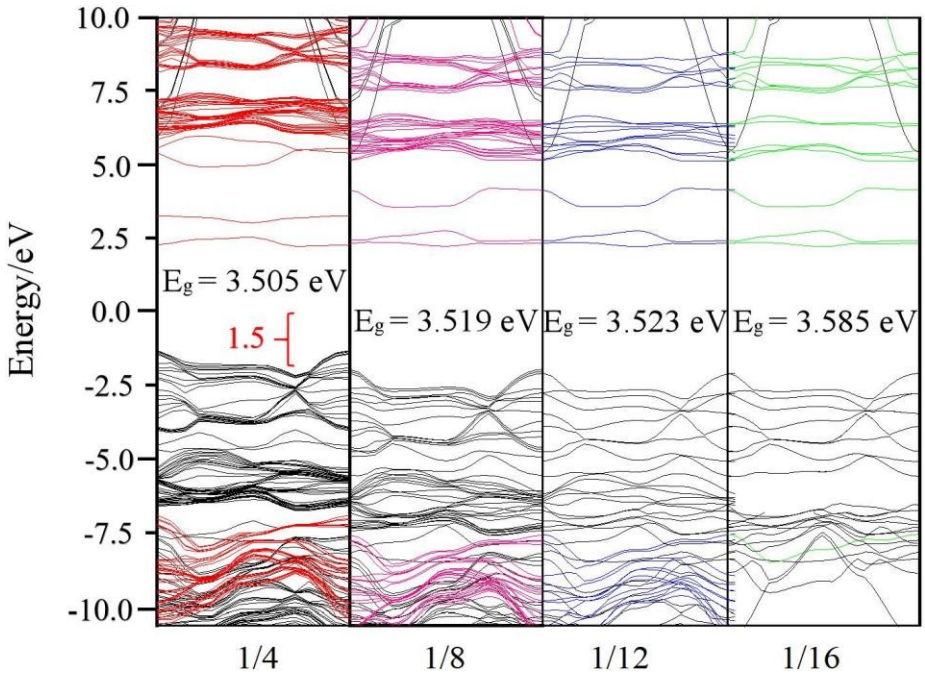


Fig. S9 Band structure of $Li(Mn_{1-x}Fe_x)PO_4$ at Fermi level