# A Systematic First-Principles Investigation of Mixed Transition Metal Olivine Phosphates $LiM_{1-y}M'_yPO_4$ (M/M'=Mn, Fe, Co) As Cathode Materials

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Supplementary material includes 9 figures, 3 tables for a total of 17 pages.

**Figure S1:** Variations of the unit cell parameters and volume of $LiFe_{1-y}Mn_yPO_4$ as a function of the composition parameter y

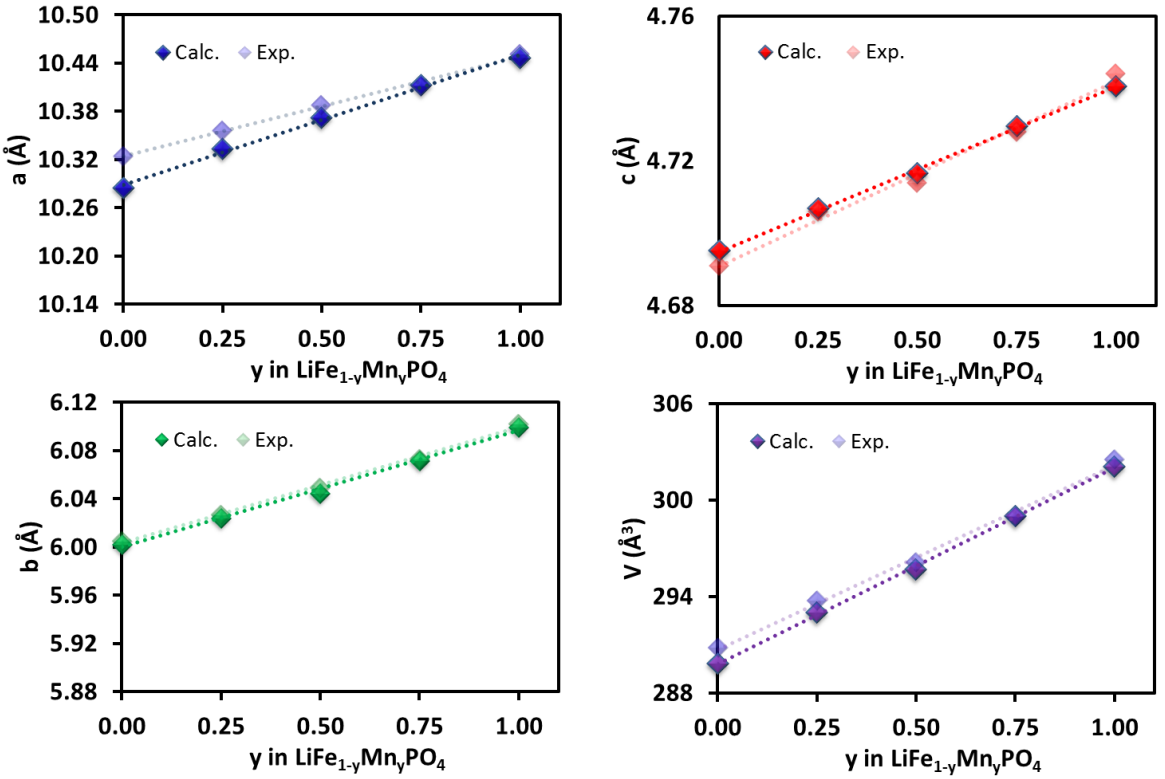
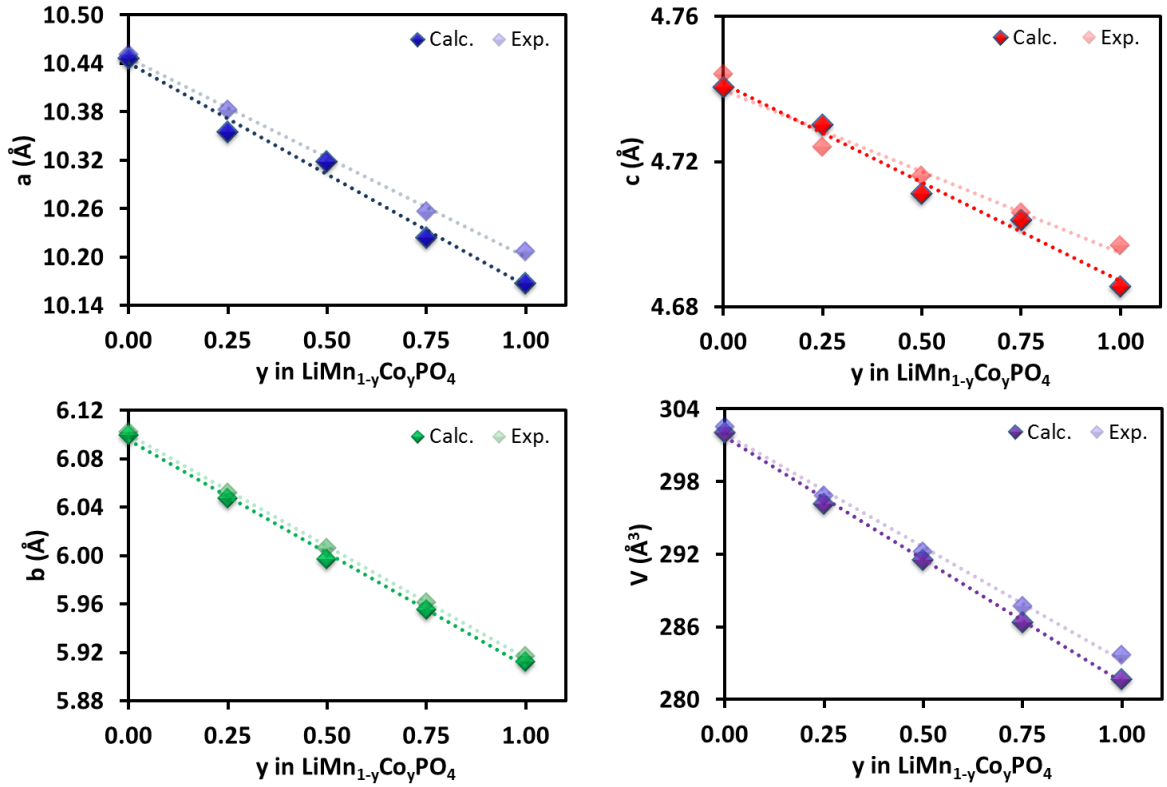



**Figure S2:** Variations of the unit cell parameters and volume of $LiMn_{1-y}Co_yPO_4$ as a function of the composition parameter y



**Figur S3:** Variations of the unit cell parameters and volume of $LiFe_{1-y}Co_yPO_4$ as a function of the composition parameter y

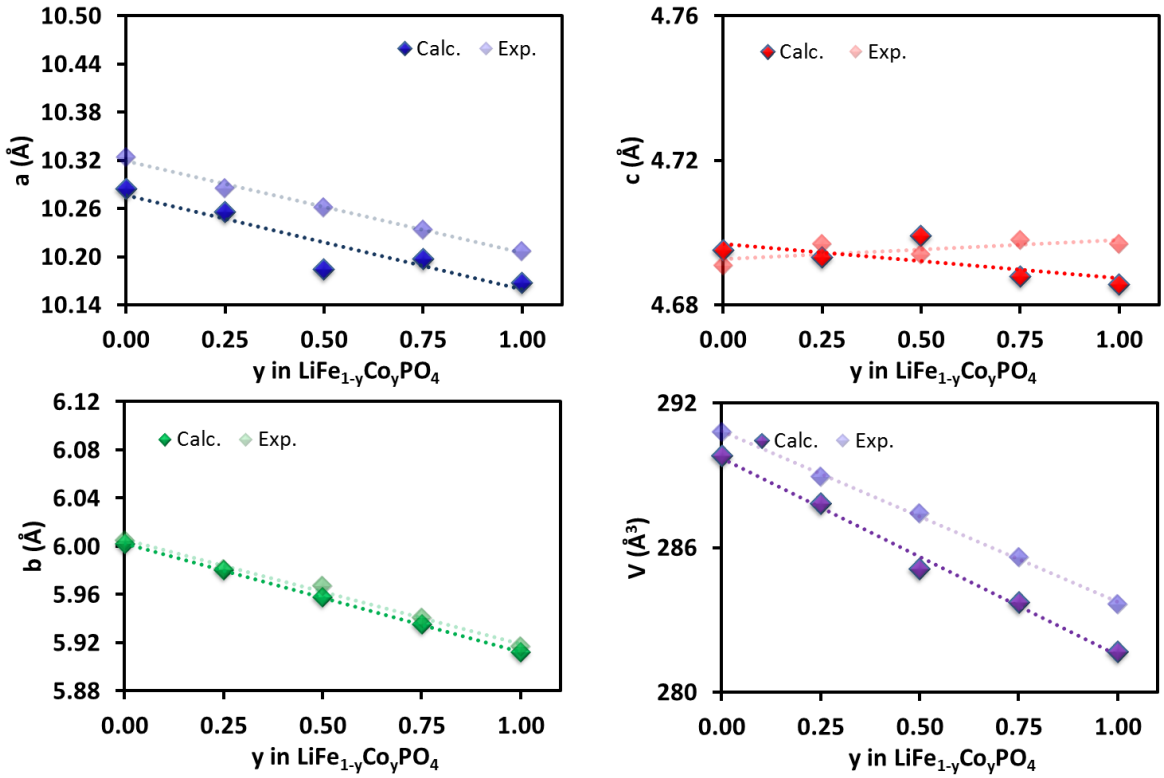
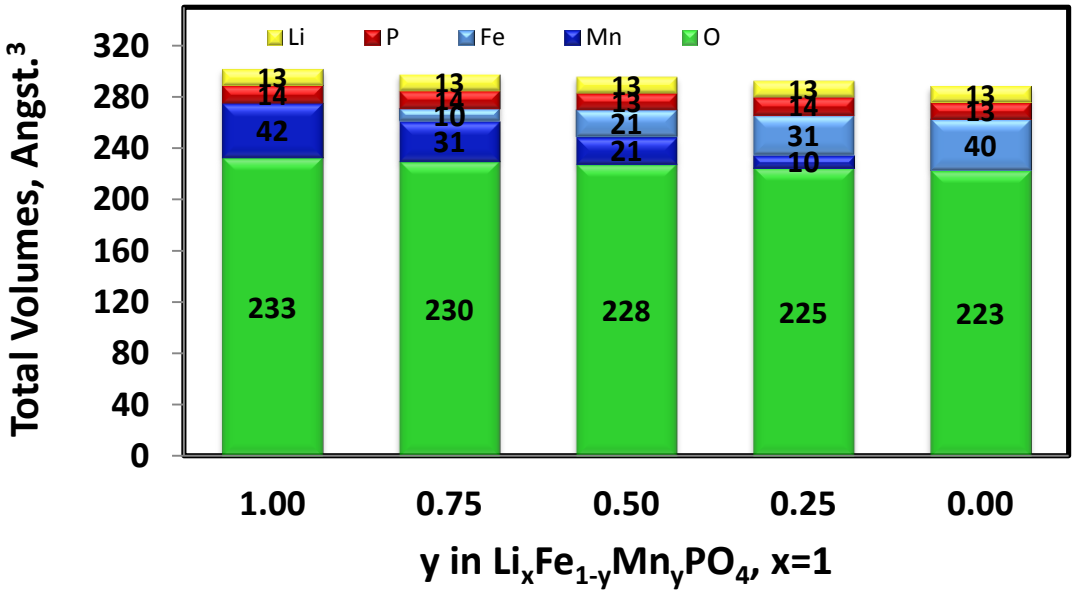
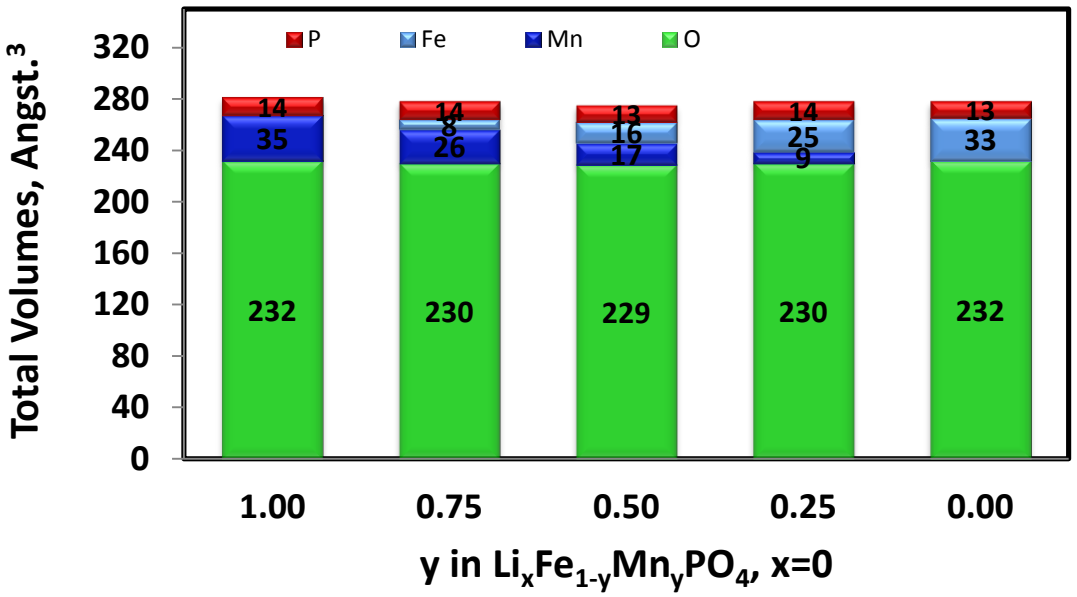


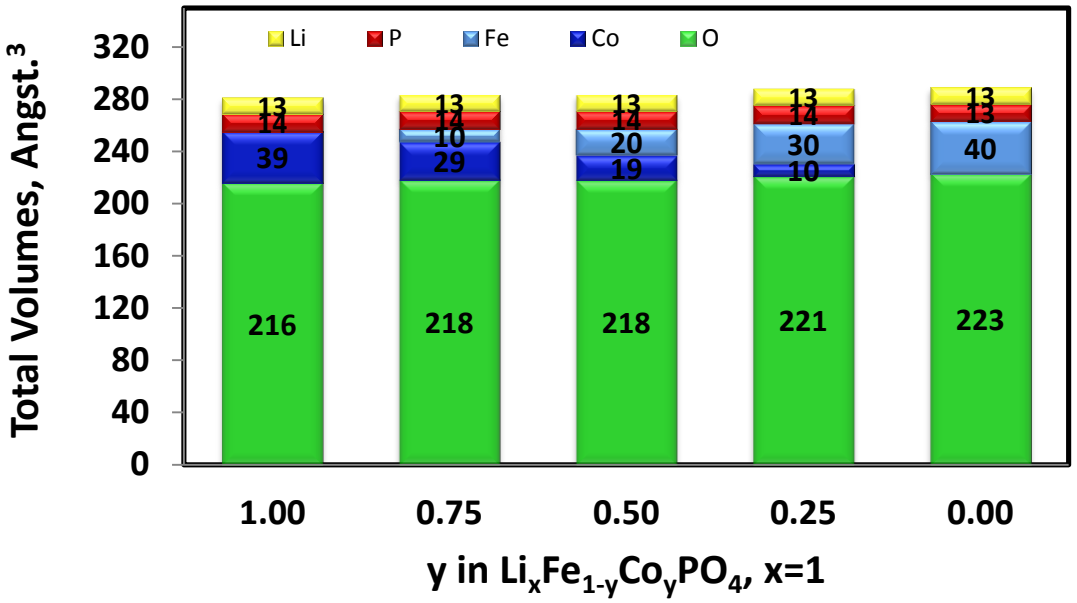

**Figure S4:** Bader volumes population evolution for mixed $Li_xM_{1-y}M_yPO_4$ olivines. (M=Co, Fe, Mn, x=1 and 0): (a) $Li_xFe_{1-y}Mn_yPO_4$; (b) $Li_xFe_{1-y}Co_yPO_4$; (c) $Li_xMn_{1-y}Co_yPO_4$

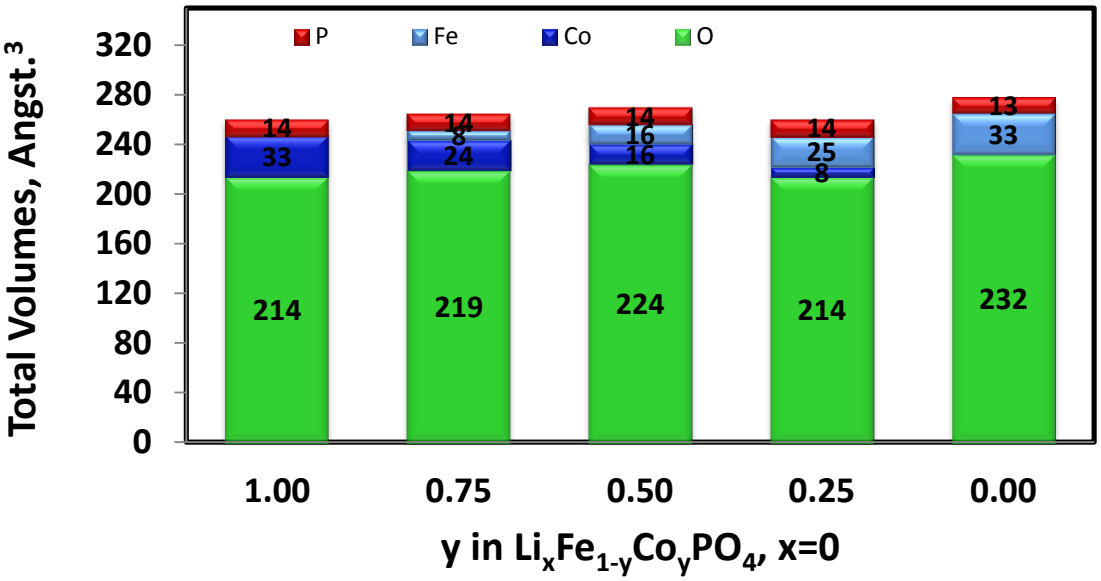
(a)



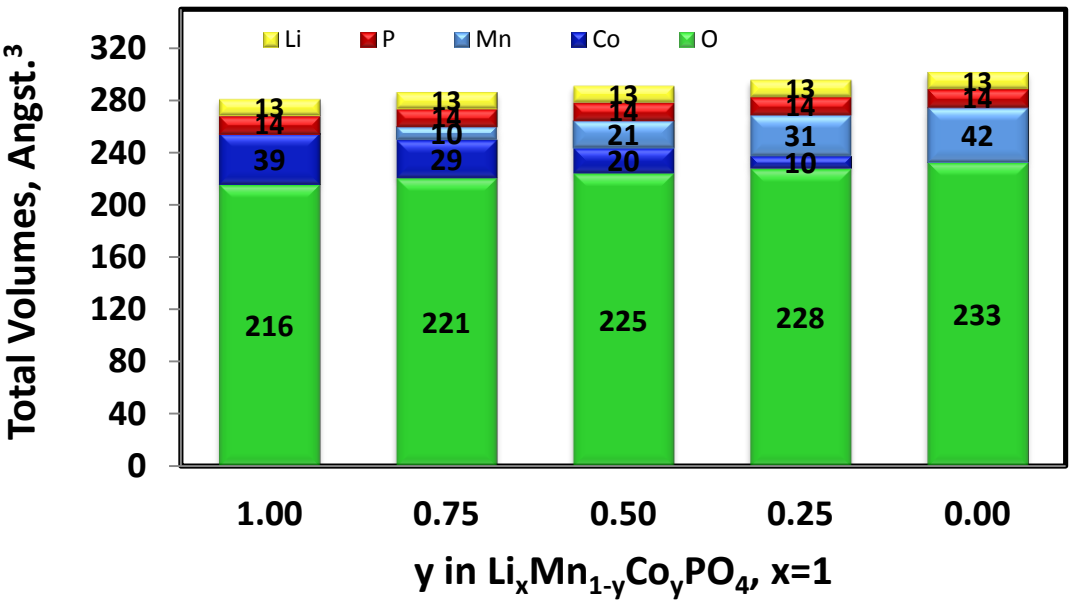

P
Fe
Mn
O
Total Volumes, Angst.3
320
280
240
200
160
120
80
40
0
14
35
232
14
8
26
230
13
16
17
229
14
25
9
230
13
33
232
1.00
0.75
0.50
0.25
0.00
y in Li$_x$Fe$_{1-y}$Mn$_y$PO$_4$, x=0

**(b)**


Li
P
Fe
Co
O
Total Volumes, Angst.3
320
280
240
200
160
120
80
40
0
13
14
39
216
13
14
10
29
218
13
14
20
19
218
13
14
30
10
221
13
13
40
223
1.00
0.75
0.50
0.25
0.00
y in Li$_x$Fe$_{1-y}$Co$_y$PO$_4$, x=1


P
Fe
Co
O
Total Volumes, Angst.3
320
280
240
200
160
120
80
40
0
14
33
214
14
8
24
219
14
16
16
224
14
25
8
214
13
33
232
1.00
0.75
0.50
0.25
0.00
y in Li$_x$Fe$_{1-y}$Co$_y$PO$_4$, x=0

(c)


Li
P
Mn
Co
O
Total Volumes, Angst.3
320
280
240
200
160
120
80
40
0
13
14
39
216
13
14
10
29
221
13
14
21
20
225
13
14
31
10
228
13
14
42
233
1.00
0.75
0.50
0.25
0.00
y in Li$_x$Mn$_{1-y}$Co$_y$PO$_4$, x=1

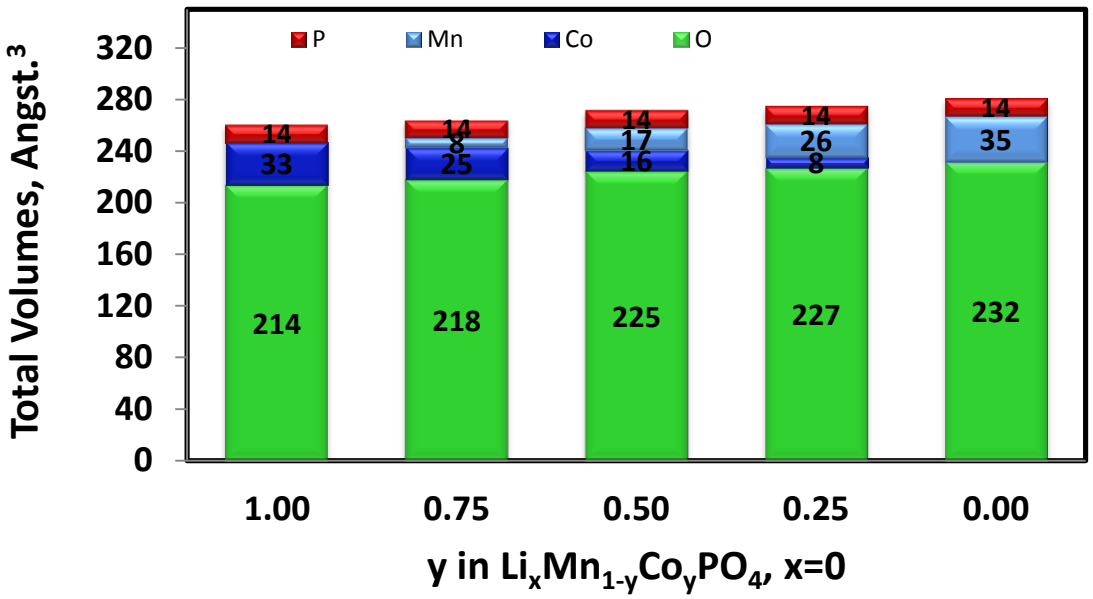



**Figure S5:** Schematic view of the octahedral $M(H_2O)_6^{2+}$ complex .The transition metal ion M (M=Co, Fe, Mn) is enclosed in octahedra of O linked by H

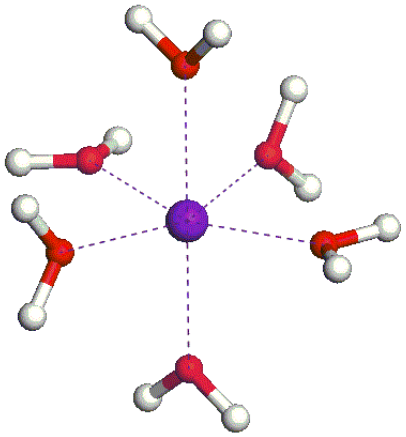


**Figure S6:** Spatial representation of HOMO orbitals of $M(H_2O)_6^{2+}$ complexes (a) M=Co (b) M=Fe (c) M= Mn

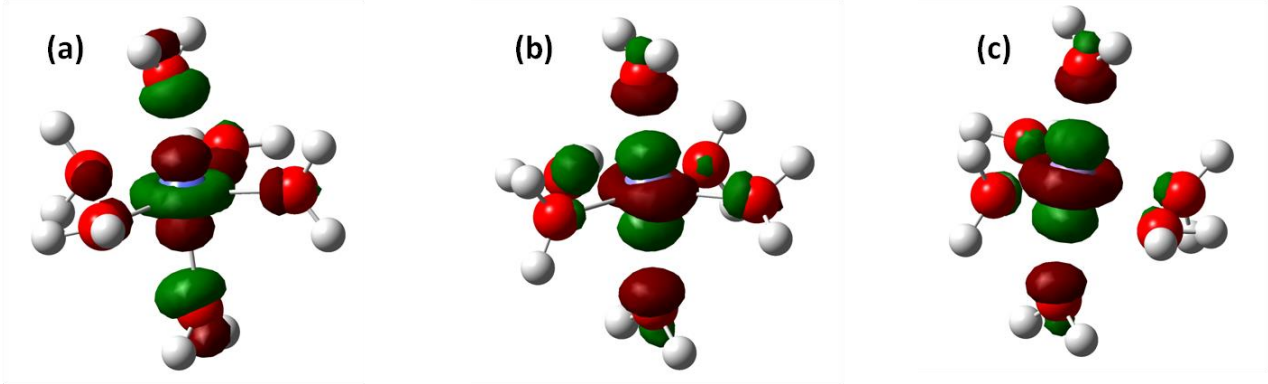
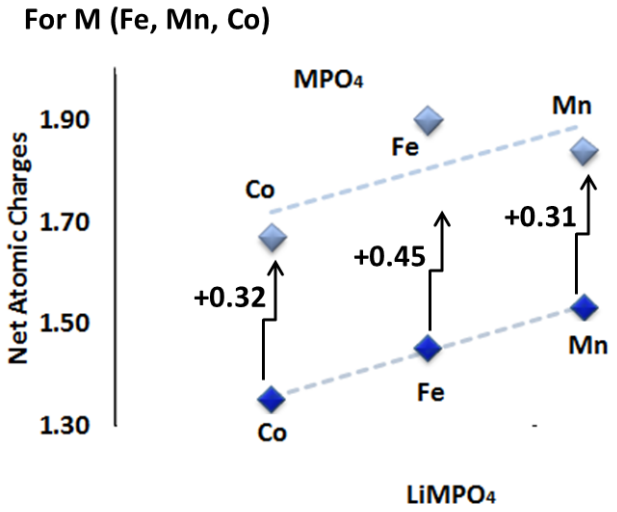
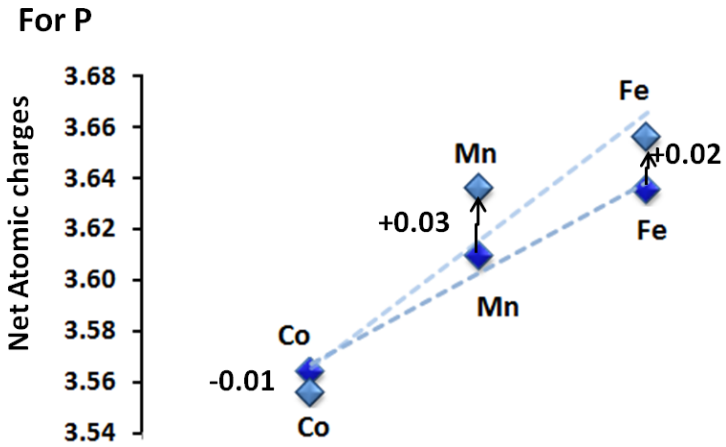


**Figure S7:** (a-c) Net atomic charges of M, P and O in $LiMPO_4$ and $MPO_4$ ( M= Fe, Co, Mn), calculated by the Bader approach.

(a)




(b)



(c)

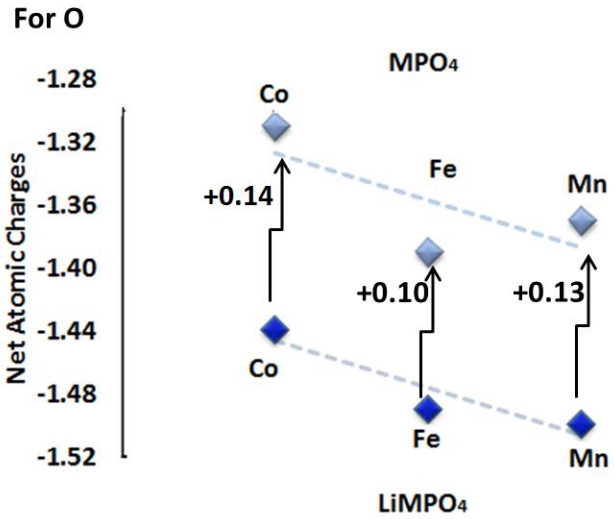
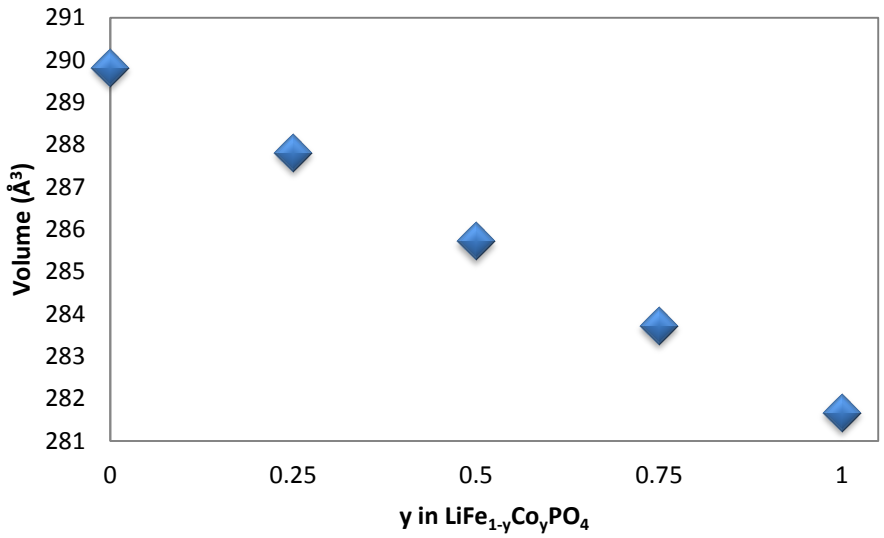
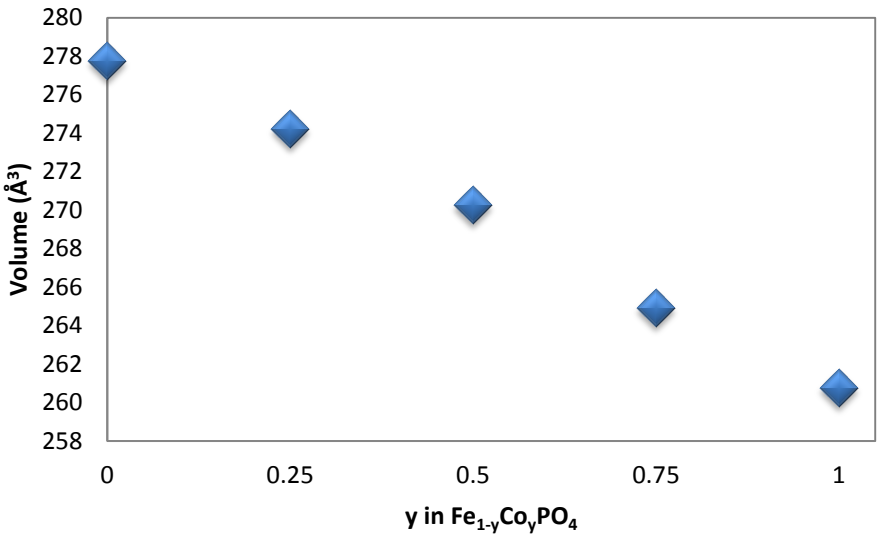



**Figure S8:** (a,b) Volume changes in lithiated (a) and delithiated (b) mixed iron cobalt olivines

(a)




(b)

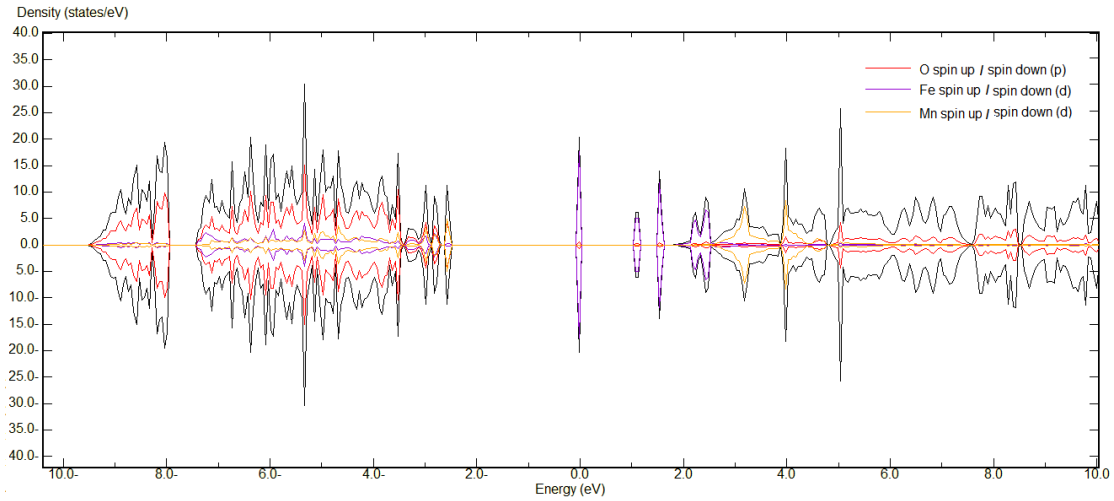

280
278
276
274
272
270
268
266
264
262
260
258
Volume (Å3)
0
0.25
0.5
0.75
1
y in Fe1-yCoyPO4

**Redox active electrons and density of states**

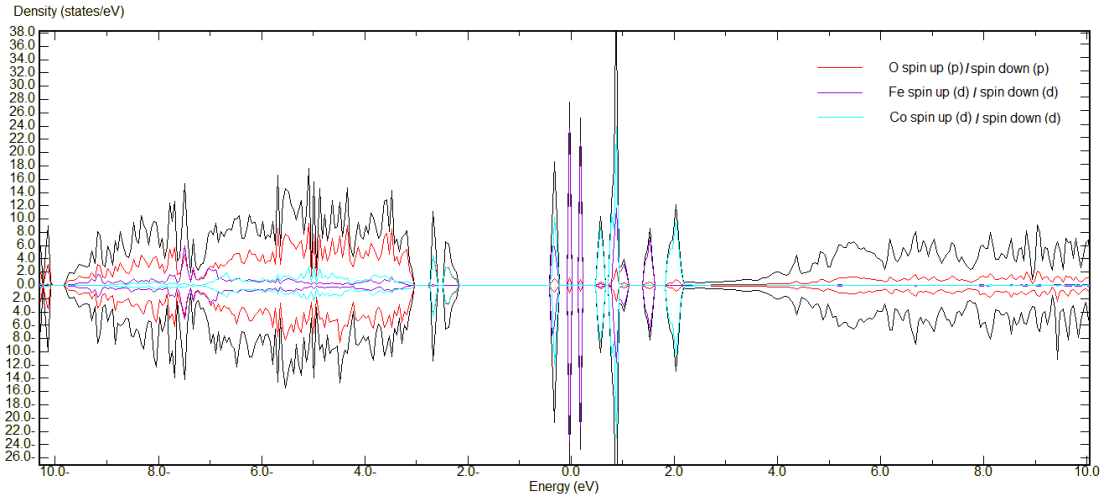
Based on the discussion on page 20-21 in the main manuscript, it is expected that in the mixed $LiM_{1-y}M'_yPO_4$ compounds the redox active electron (i.e. the top of the valence band) should belong to the metal with the highest d-band energy. The mixed electronic DOS of both $LiFe_{0.5}Mn_{0.5}PO_4$ and $LiFe_{0.5}Co_{0.5}PO_4$ indicate that the top of the valence band belongs to the d-states of the iron, indicated in cyan, Figure S9a and s9b, in qualitative agreement with the computed and experimental redox potentials (Figure 6a and 6b). However, for the $LiMn_{0.5}Co_{0.5}PO_4$ compound we did not succeed in reproducing the correct d-band ordering resulting in the Co d-electrons populating the top of the valence band (Figure S9c).

**Figure S9:** Calculated density of states for (a) $LiFe_{0.5}Mn_{0.5}PO_4$; (b) $LiFe_{0.5}Co_{0.5}PO_4$; (c)$LiMn_{0.5}Co_{0.5}PO_4$

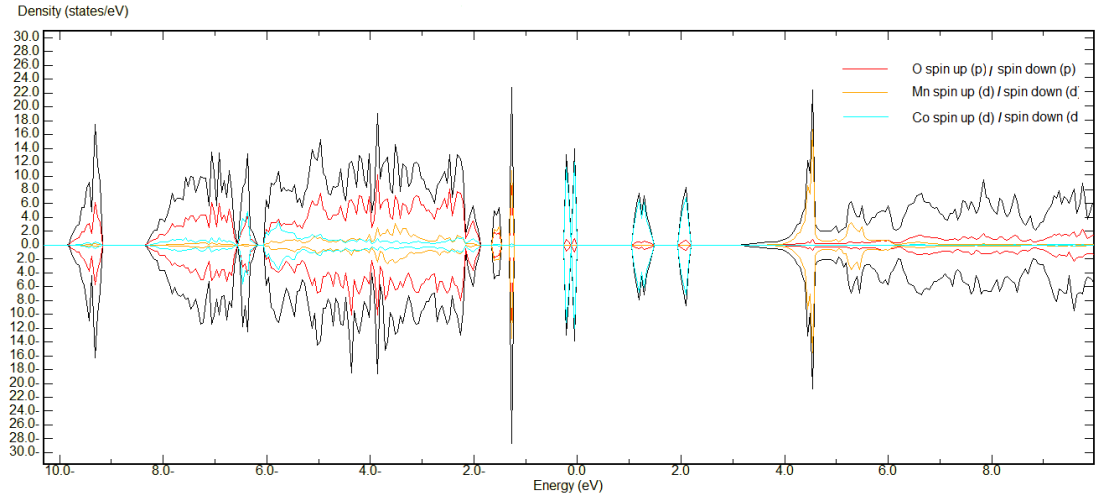
(a)



(b)




(c)




However, a recent study by Johannes et. al[1] suggests that the GGA+U level might not be sufficiently accurate to describe the fine electronic structure details such as the composition of the top of the valence band, as compared to a hybrid functional such as HSE06. See Table 1 in the aforementioned reference and the discussion therein. On the other hand, the scheme developed by Ceder et. al.[2] for computing the voltage of these compounds is based on total energy calculations with suitable Hubbard

parameters, thus resulting in a good agreement with the experimental findings at the GGA+U level of theory.

**Table S1:** Calculated and experimental cell parameters of the olivine structures in the lithiated state, as well as discrepancy between the theoretical and experimental values

| system | x | Calculated (GGA+U) | | | | Experimental | | | | % (Calc. vs Exp.) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | a(Å) | b(Å) | c(Å) | V (Å$^3$) | a(Å) | b(Å) | c(Å) | V(Å$^3$) | a(Å) | b(Å) | c(Å) | V(Å$^3$) |
| $LiFe_{1-x}Mn_xPO_4$ | **1.00** | 10.447 | 6.099 | 4.741 | 302.060 | 10.451 | 6.102 | 4.744 | 302.530 | 0.042 | 0.043 | 0.070 | 0.155 |
| | **0.75** | 10.412 | 6.072 | 4.730 | 299.000 | 10.412 | 6.073 | 4.728 | 298.960 | 0.001 | 0.022 | 0.032 | 0.013 |
| | **0.50** | 10.372 | 6.044 | 4.717 | 295.690 | 10.388 | 6.049 | 4.714 | 296.100 | 0.155 | 0.078 | 0.056 | 0.138 |
| | **0.25** | 10.333 | 6.024 | 4.707 | 292.980 | 10.356 | 6.027 | 4.706 | 293.730 | 0.224 | 0.050 | 0.019 | 0.255 |
| | **0.00** | 10.285 | 6.002 | 4.695 | 289.830 | 10.324 | 6.005 | 4.691 | 290.820 | 0.380 | 0.047 | 0.086 | 0.340 |
| $LiMn_{1-x}Co_xPO_4$ | **1.00** | 10.168 | 5.912 | 4.686 | 281.680 | 10.207 | 5.917 | 4.697 | 283.670 | 0.385 | 0.080 | 0.240 | 0.702 |
| | **0.75** | 10.224 | 5.955 | 4.704 | 286.370 | 10.257 | 5.961 | 4.706 | 287.730 | 0.322 | 0.101 | 0.042 | 0.473 |
| | **0.50** | 10.318 | 5.997 | 4.711 | 291.530 | 10.318 | 6.006 | 4.716 | 292.250 | -0.001 | 0.149 | 0.100 | 0.246 |
| | **0.25** | 10.355 | 6.047 | 4.730 | 296.210 | 10.383 | 6.052 | 4.724 | 296.840 | 0.270 | 0.076 | 0.130 | 0.212 |
| | **0.00** | 10.447 | 6.099 | 4.741 | 302.060 | 10.451 | 6.102 | 4.744 | 302.530 | 0.042 | 0.043 | 0.070 | 0.155 |
| $LiFe_{1-x}Co_xPO_4$ | **1.00** | 10.168 | 5.912 | 4.686 | 281.680 | 10.207 | 5.917 | 4.697 | 283.670 | 0.385 | 0.080 | 0.240 | 0.702 |
| | **0.75** | 10.198 | 5.935 | 4.688 | 283.730 | 10.234 | 5.941 | 4.698 | 285.630 | 0.356 | 0.099 | 0.215 | 0.665 |
| | **0.50** | 10.184 | 5.958 | 4.699 | 285.130 | 10.262 | 5.967 | 4.694 | 287.420 | 0.756 | 0.154 | 0.109 | 0.797 |
| | **0.25** | 10.255 | 5.980 | 4.693 | 287.820 | 10.286 | 5.981 | 4.697 | 288.960 | 0.298 | 0.015 | 0.083 | 0.395 |
| | **0.00** | 10.285 | 6.002 | 4.695 | 289.830 | 10.324 | 6.005 | 4.691 | 290.820 | 0.380 | 0.047 | 0.086 | 0.340 |

**Table S2:** Calculated average metal-O ($MO_6$ octahedra) bond lengths in $Li_xM_{1-y}M_yPO_4$ olivines (M = Fe, Co, Mn; y=1, 0.75, 0.5, 0.25, 0 and x=1, y, 0)
**(a)**

| | y | Mn-O(Å) | | | | | | Co-O(Å) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ |
| $LiMn_{1-y}Co_yPO_4$ | 1 | | | | | | | 2.110 | 2.072 | 2.177 | 2.177 | 2.054 | 2.054 |
| | 0.75 | 2.210 | 2.126 | 2.251 | 2.251 | 2.112 | 2.112 | 2.120 | 2.066 | 2.170 | 2.170 | 2.072 | 2.072 |
| | 0.5 | 2.236 | 2.142 | 2.249 | 2.249 | 2.115 | 2.115 | 2.110 | 2.068 | 2.189 | 2.189 | 2.072 | 2.072 |
| | 0.25 | 2.228 | 2.136 | 2.255 | 2.255 | 2.123 | 2.123 | 2.142 | 2.050 | 2.167 | 2.167 | 2.113 | 2.113 |
| | 0 | 2.237 | 2.144 | 2.264 | 2.264 | 2.132 | 2.132 | | | | | | |
| $Mn_{1-y}Co_yPO_4$ | 1 | | | | | | | 1.917 | 1.911 | 2.144 | 2.144 | 1.943 | 1.943 |
| | 0.75 | 1.901 | 1.884 | 2.056 | 2.056 | 1.985 | 1.985 | 1.898 | 1.916 | 2.131 | 2.131 | 2.020 | 2.020 |
| | 0.5 | 1.879 | 1.889 | 1.992 | 1.992 | 2.280 | 2.280 | 1.852 | 1.848 | 2.089 | 2.089 | 2.081 | 2.081 |
| | 0.25 | 1.891 | 1.880 | 2.270 | 2.270 | 2.003 | 2.003 | 1.863 | 1.843 | 2.140 | 2.140 | 2.049 | 2.049 |
| | 0 | 1.889 | 1.883 | 2.310 | 2.310 | 1.996 | 1.996 | | | | | | |
| $Li_{x=y}Mn_{1-y}Co_yPO_4$ | 0.75 | 1.938 | 1.915 | 2.251 | 2.096 | 2.087 | 1.974 | 2.203 | 2.009 | 2.291 | 2.233 | 2.034 | 2.011 |
| | 0.25 | 1.927 | 1.882 | 2.337 | 2.272 | 2.016 | 1.965 | 2.026 | 1.964 | 2.196 | 2.161 | 2.128 | 2.082 |
| | 0.5 | 1.939 | 1.887 | 2.296 | 2.265 | 2.024 | 1.964 | 2.041 | 2.028 | 2.296 | 2.115 | 2.136 | 2.041 |

**(b)**

| | y | Fe-O(Å) | | | | | | Co-O(Å) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ |
| $LiFe_{1-y}Co_yPO_4$ | 1 | | | | | | | 2.110 | 2.072 | 2.177 | 2.177 | 2.054 | 2.054 |
| | 0.75 | 2.099 | 2.168 | 2.223 | 2.223 | 2.055 | 2.055 | 2.074 | 2.115 | 2.182 | 2.182 | 2.056 | 2.056 |
| | 0.5 | 2.094 | 2.176 | 2.230 | 2.230 | 2.057 | 2.057 | 2.086 | 2.117 | 2.184 | 2.184 | 2.055 | 2.055 |
| | 0.25 | 2.102 | 2.180 | 2.232 | 2.232 | 2.059 | 2.059 | 2.079 | 2.121 | 2.193 | 2.193 | 2.058 | 2.058 |
| | 0 | 2.103 | 2.185 | 2.236 | 2.236 | 2.059 | 2.059 | | | | | | |
| $Fe_{1-y}Co_yPO_4$ | 1 | | | | | | | 1.917 | 1.911 | 2.144 | 2.144 | 1.943 | 1.943 |
| | 0.75 | 1.918 | 1.905 | 2.140 | 2.140 | 2.021 | 2.021 | 1.910 | 1.895 | 2.121 | 2.121 | 1.982 | 1.982 |
| | 0.5 | 1.941 | 1.927 | 2.117 | 2.117 | 2.018 | 2.018 | 1.909 | 1.907 | 2.170 | 2.170 | 1.958 | 1.958 |
| | 0.25 | 1.931 | 1.917 | 2.121 | 2.121 | 2.039 | 2.039 | 1.865 | 1.855 | 2.113 | 2.113 | 2.060 | 2.060 |
| | 0 | 1.932 | 1.921 | 2.129 | 2.129 | 2.041 | 2.041 | | | | | | |
| $Li_{x=y}Fe_{1-y}Co_yPO_4$ | 0.75 | 1.990 | 1.966 | 2.086 | 2.055 | 2.044 | 2.019 | 2.156 | 2.008 | 2.241 | 2.195 | 2.062 | 2.038 |
| | 0.5 | 1.996 | 1.901 | 2.133 | 2.109 | 2.071 | 2.012 | 2.089 | 2.036 | 2.298 | 2.105 | 2.087 | 2.022 |
| | 0.25 | 1.992 | 1.923 | 2.141 | 2.111 | 2.041 | 1.997 | 2.050 | 1.957 | 2.165 | 2.163 | 2.117 | 2.094 |

**(c)**

| | y | Fe-O(Å) | | | | | | Mn-O(Å) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ | O1 | O2 | O3 | O3 | $O_3'$ | $O_3'$ |
| $LiFe_{1-y}Mn_yPO_4$ | 1 | | | | | | | 2.237 | 2.144 | 2.264 | 2.264 | 2.132 | 2.132 |
| | 0.75 | 2.200 | 2.108 | 2.236 | 2.236 | 2.077 | 2.077 | 2.236 | 2.140 | 2.263 | 2.263 | 2.126 | 2.126 |
| | 0.5 | 2.182 | 2.095 | 2.243 | 2.243 | 2.070 | 2.070 | 2.246 | 2.148 | 2.251 | 2.251 | 2.118 | 2.118 |
| | 0.25 | 2.191 | 2.106 | 2.236 | 2.236 | 2.065 | 2.065 | 2.229 | 2.133 | 2.260 | 2.260 | 2.116 | 2.116 |
| | 0 | 2.185 | 2.103 | 2.236 | 2.236 | 2.059 | 2.059 | | | | | | |
| $Fe_{1-y}Mn_yPO_4$ | 1 | | | | | | | 1.889 | 1.883 | 2.310 | 2.310 | 1.996 | 1.996 |
| | 0.75 | 1.925 | 1.912 | 2.157 | 2.157 | 2.034 | 2.034 | 1.897 | 1.880 | 2.291 | 2.291 | 2.003 | 2.003 |
| | 0.5 | 1.935 | 1.922 | 2.160 | 2.160 | 2.117 | 2.117 | 1.932 | 1.906 | 2.377 | 2.377 | 2.002 | 2.002 |
| | 0.25 | 1.926 | 1.925 | 2.135 | 2.135 | 2.038 | 2.038 | 1.907 | 1.875 | 2.273 | 2.273 | 2.009 | 2.009 |
| | 0 | 1.932 | 1.921 | 2.129 | 2.129 | 2.041 | 2.041 | | | | | | |
| $Li_{x=y}Fe_{1-y}Mn_yPO_4$ | 0.75 | 2.215 | 2.107 | 2.272 | 2.234 | 2.140 | 2.128 | 1.997 | 1.925 | 2.180 | 2.134 | 2.127 | 2.028 |
| | 0.25 | 2.139 | 2.102 | 2.268 | 2.255 | 2.168 | 2.097 | 2.001 | 1.966 | 2.143 | 2.067 | 2.068 | 2.000 |
| | 0.5 | 2.137 | 2.133 | 2.319 | 2.289 | 2.101 | 2.045 | 1.992 | 2.062 | 2.117 | 2.056 | 1.958 | 2.048 |

**Table S3:** The FFT grid specification and Bader charge and volume analysis for $LiMPO_4$ (M=Co, Fe, Mn) systems.

**$LiCoPO_4$**

| Atom Name | FFT grid | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NGX=40 NGY = 24 NGZ = 18 NGXF=80 NGYF=48 NGZF= 6 | | NGX =80 NGY =48 NGZ =36 NGXF= 160 NGYF=96 NGZF=72 | | NGX =120 NGY =72 NGZ =54 NGXF=240 NGYF=160 NGZF=108 | | NGX =80 NGY =72 NGZ =54 NGXF=320 NGYF=192 NGZF=144 | |
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| Li | 0.87 | 12.76 | 0.87 | 12.52 | 0.87 | 12.49 | 0.87 | 12.47 |
| O | -1.42 | 212.66 | -1.47 | 217.28 | -1.48 | 217.97 | -1.48 | 218.21 |
| P | 3.48 | 15.14 | 3.64 | 13.38 | 3.67 | 12.91 | 3.68 | 12.74 |
| Co | 1.31 | 41.12 | 1.36 | 38.49 | 1.36 | 38.31 | 1.36 | 38.26 |

**$CoPO_4$**

| Atom Name | FFT grid | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NGX=36 NGY = 24 NGZ = 18 NGXF=72 NGYF=42 NGZF=3 6 | | NGX =72 NGY =42 NGZ =36 NGXF= 144 NGYF=84 NGZF=72 | | NGX =72 NGY =24 NGZ =18 NGXF=216 NGYF=126 NGZF=108 | | NGX =72 NGY =42 NGZ =36 NGXF=288 NGYF=168 NGZF=144 | |
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| O | -1.28 | 212.46 | -1.33 | 214.80 | -1.33 | 214.68 | -1.34 | 215.94 |
| P | 3.50 | 14.70 | 3.63 | 13.53 | 3.67 | 12.70 | 3.69 | 12.72 |
| Co | 1.63 | 32.43 | 1.67 | 32.43 | 1.65 | 33.39 | 1.68 | 32.12 |

**$LiFePO_4$**

| Atom Name | FFT grid | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NGX=40 NGY = 24 NGZ = 18 NGXF=80 NGYF=48 NGZF=3 6 | | NGX =80 NGY =48 NGZ =36 NGXF= 160 NGYF=96 NGZF=72 | | NGX =120 NGY =72 NGZ =54 NGXF=240 NGYF=160 NGZF=108 | | NGX =80 NGY =96 NGZ =72 NGXF=320 NGYF=192 NGZF=144 | |
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| Li | 0.87 | 12.87 | 0.87 | 12.76 | 0.87 | 12.69 | 0.87 | 12.68 |
| O | -1.44 | 218.95 | -1.49 | 223.06 | -1.50 | 223.82 | -1.50 | 224.06 |
| P | 3.48 | 15.09 | 3.63 | 13.48 | 3.67 | 12.92 | 3.68 | 12.75 |
| Fe | 1.40 | 42.92 | 1.45 | 40.52 | 1.45 | 40.40 | 1.45 | 40.35 |

**$FePO_4$**

| Atom Name | FFT grid | | | |
|---|---|---|---|---|
| | NGX=36 NGY = 21 NGZ = 18 | NGX =72 NGY =42 NGZ =36 | NGX =72 NGY =64 NGZ =54 | NGX =72 NGY =96 NGZ =72 |

| | NGXF=72 NGYF=42 NGZF=3 6 | | NGXF= 144 NGYF=84 NGZF=72 | | NGXF=216 NGYF=126 NGZF=108 | | NGXF=288 NGYF=168 NGZF=144 | |
|---|---|---|---|---|---|---|---|---|
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| O | -1.34 | 227.49 | -1.38 | 231.10 | -1.40 | 232.31 | -1.40 | 232.46 |
| P | 3.52 | 14.74 | 3.62 | 13.70 | 3.69 | 14.74 | 3.70 | 12.74 |
| Fe | 1.84 | 35.51 | 1.90 | 32.94 | 1.90 | 35.51 | 1.91 | 32.55 |

**$LiMnPO_4$**

| **Atom Name** | **FFT grid** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NGX=40 NGY = 24 NGZ = 18 NGXF=80 NGYF=48 NGZF=3 6 | | NGX =80 NGY =48 NGZ =36 NGXF= 160 NGYF=96 NGZF=72 | | NGX =80 NGY =48 NGZ =36 NGXF=240 NGYF=160 NGZF=108 | | NGX =80 NGY =48 NGZ =36 NGXF=320 NGYF=192 NGZF=144 | |
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| Li | 0.85 | 14.22 | 0.87 | 12.93 | 0.87 | 12.85 | 0.87 | 12.84 |
| O | -1.45 | 227.30 | -1.51 | 233.26 | -1.52 | 234.08 | -1.52 | 234.31 |
| P | 3.44 | 15.94 | 3.62 | 13.65 | 3.66 | 13.09 | 3.68 | 12.90 |
| Mn | 1.49 | 44.55 | 1.53 | 42.16 | 1.53 | 41.97 | 1.53 | 41.94 |

**$MnPO_4$**

| **Atom Name** | **FFT grid** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NGX=36 NGY = 21 NGZ = 18 NGXF=72 NGYF=42 NGZF=3 6 | | NGX =72 NGY =48 NGZ =36 NGXF= 144 NGYF=96 NGZF=72 | | NGX =72 NGY =48 NGZ =36 NGXF=216 NGYF=144 NGZF=108 | | NGX =80 NGY =96 NGZ =72 NGXF=320 NGYF=192 NGZF=144 | |
| | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume | Average charge | Total volume |
| O | -1.32 | 228.37 | -1.37 | 231.61 | -1.38 | 232.50 | -1.39 | 232.84 |
| P | 3.46 | 16.00 | 3.63 | 13.66 | 3.69 | 12.94 | 3.71 | 12.67 |
| Mn | 1.82 | 36.02 | 1.84 | 35.13 | 1.85 | 34.95 | 1.85 | 34.88 |

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