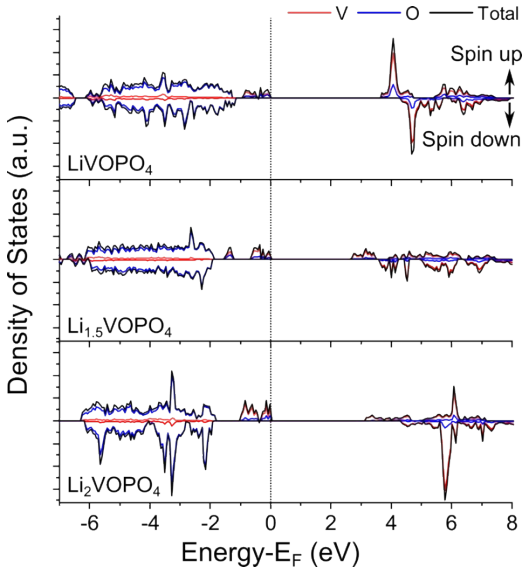
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

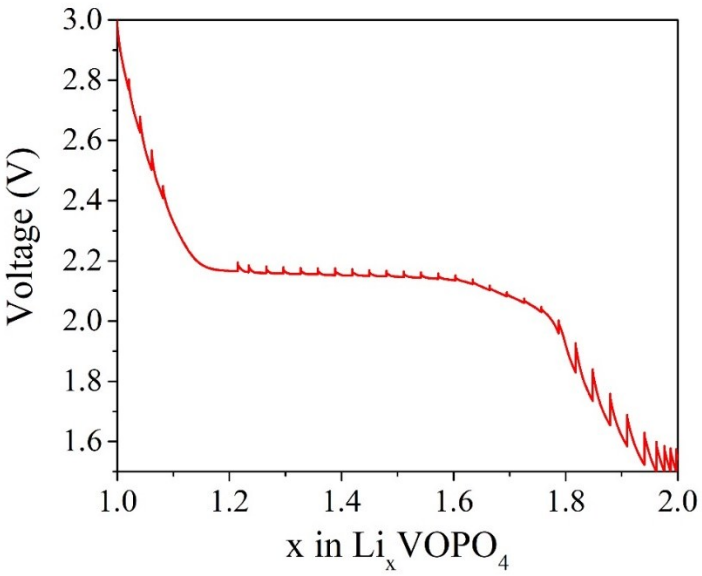
Evolution of lithium ordering with (de)-lithiation in β-$LiVOPO_4$: Insights through solid state NMR and first principles DFT calculations

Supporting Information

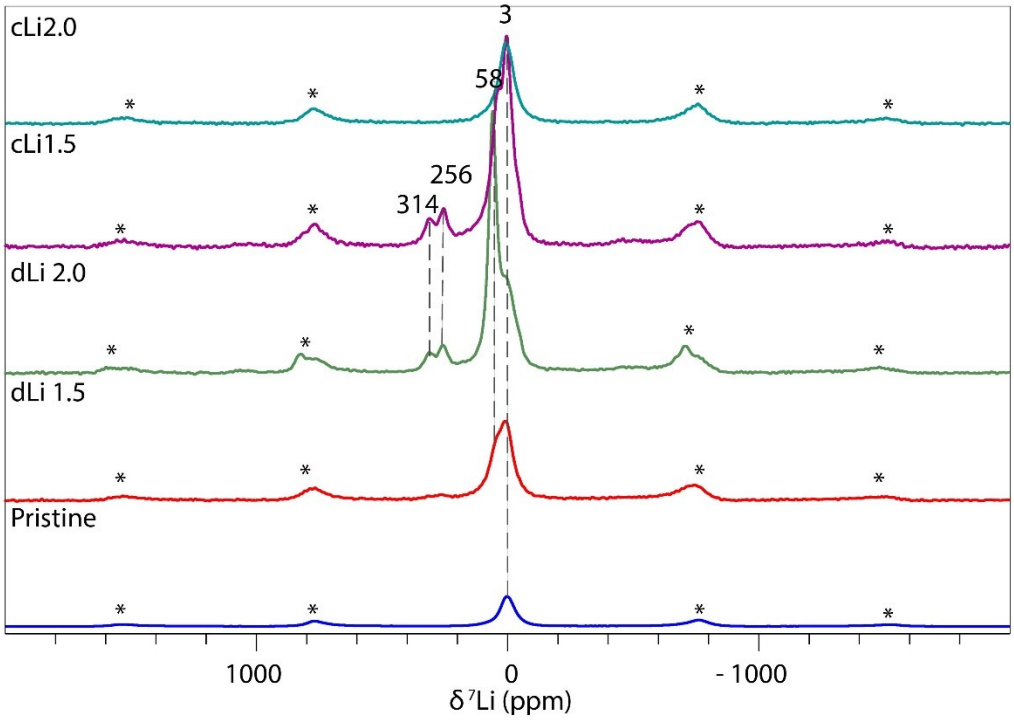
SI. 1. Density of states plot for lowest energy Li_xVOPO_4 (x=1, 1.5 and 2) structures optimized with the PBE0 hybrid functional. Energy is plotted relative to the Fermi energy (E_F) for each structure.



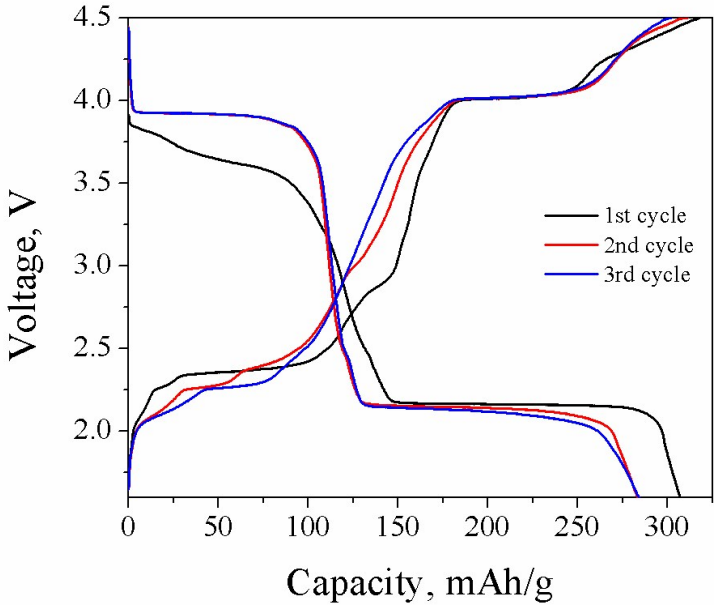
SI. 2. Galvanostatic Intermittent Titration Technique (GITT) curve of the first discharge of β-$LiVOPO_4$ at a rate of C/100 with 100 hours of rest between each ~0.03 Li increment.



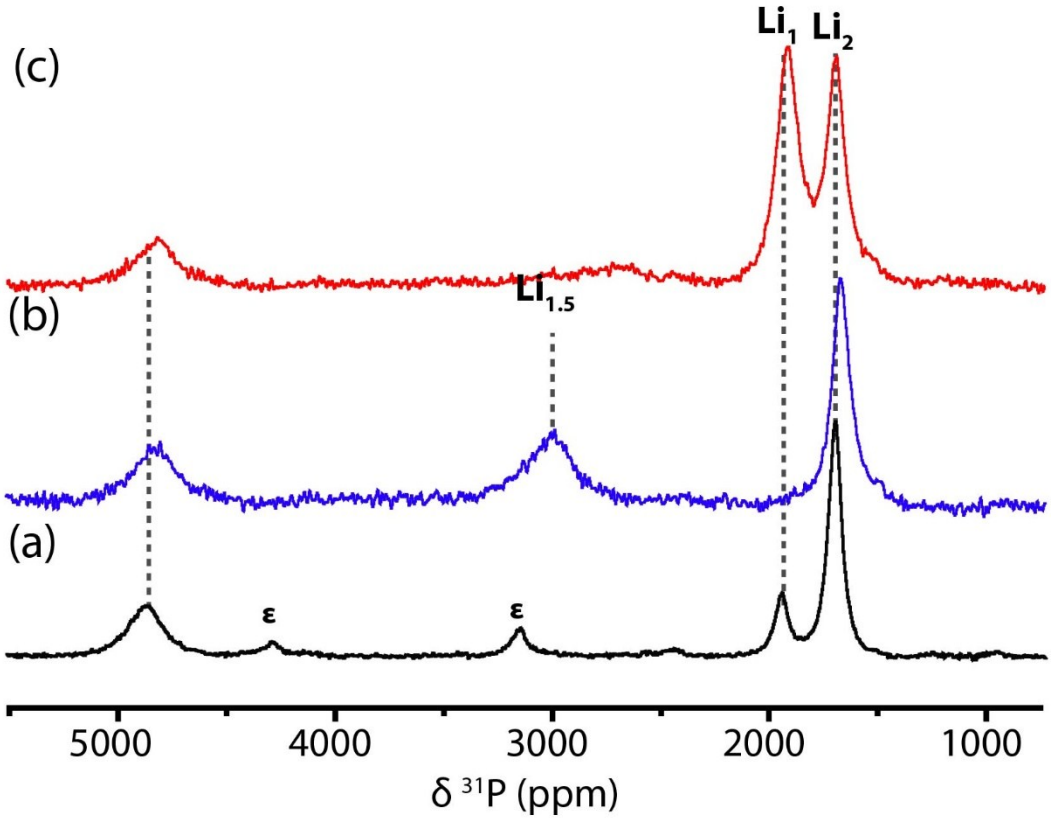
SI. 3. ^{7}Li NMR spectra of β-$LiVOPO_4$ cycled to different states of charge (SOC) in the lower voltage region between 2.4 V and 1.5 V. The spectra are scaled by mass and number of scans. The points in the galvanostatic discharge curve at which the NMR spectra were acquired are as marked in Figure 3. The spectra were acquired at a MAS frequency of 60 kHz at 4.7 T.



SI. 4. Electrochemical charge-discharge curve of β-VOPO4 derived from tetragonal H_2VOPO_4.



SI. 5. ^{31}P NMR spectrum of (a) chemically-lithiated β-Li_2VOPO_4, compared with (b) electrochemically-lithiated β-Li_2VOPO_4 discharged to 1.6 V, and (c) electrochemically-lithiated β-Li_2VOPO_4 (sample corresponding to that shown in (b)) after 3 months. The minor peaks at ~4300 ppm and 3200 pppm in the spectrum of chemically-lithiated β-Li_2VOPO_4 (labelled as ε) are assigned to an ε-Li_2VOPO_4 impurity.



SI. 6. Calculated X-ray diffraction patterns (Cu Kα radiation) of (a) β-$Li_{1.5}VOPO_4$, (b) the lowest energy structure of β-Li_2VOPO_4(str 1) and (c) a slightly higher energy ordering of β-Li_2VOPO_4 (str 2). These structures are obtained after optimisation with PBE0 functional.

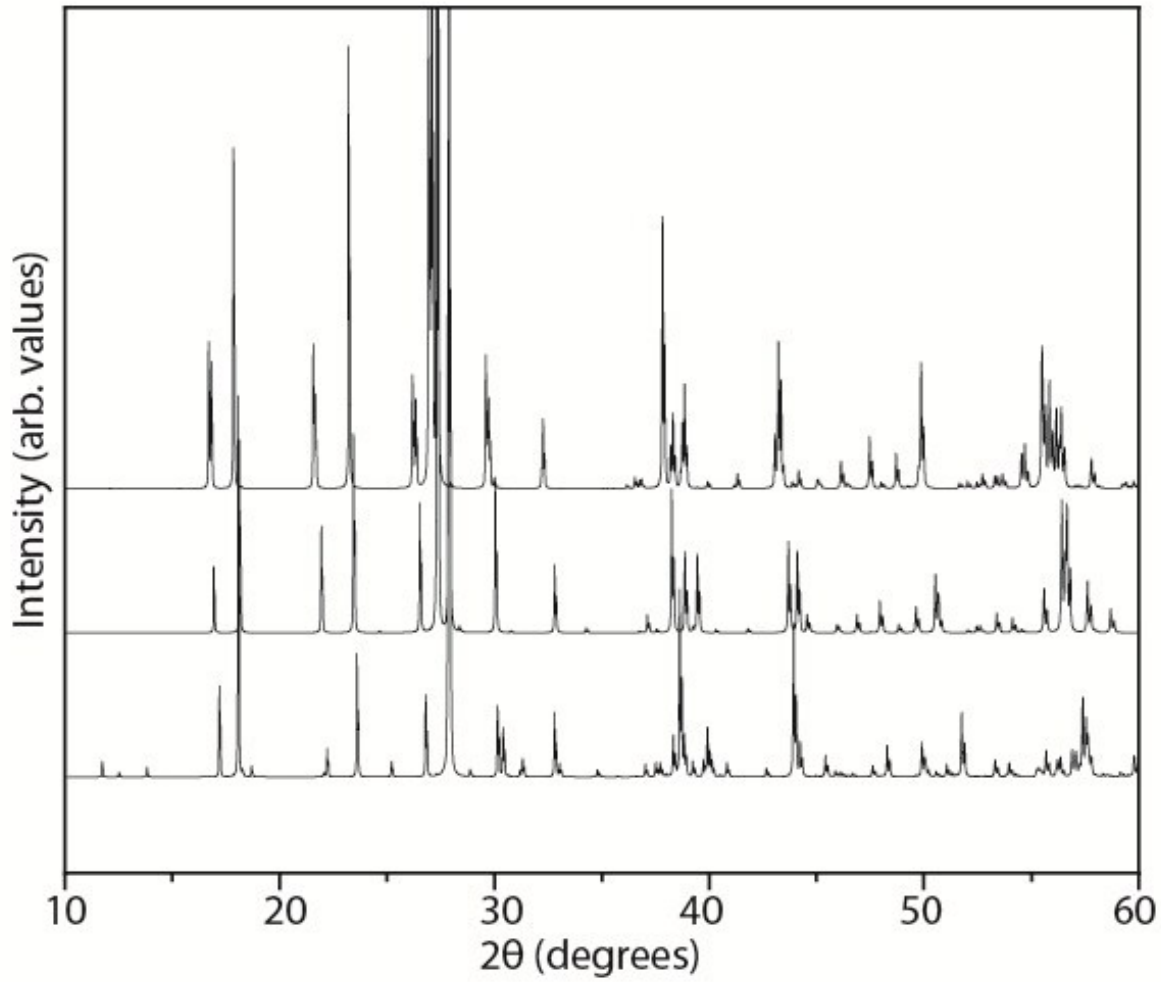


Table SI. 1. Structure of $LiVOPO_4$ optimised with PBE0 functional. a=7.351 Å, b=6.279 Å, c=7.147 Å, α=90.00°, β=90.00° and γ=90.00°.

Atom	Fractional Coordinate		
	x	y	z
Li	-0.500	0.000	0.000
Li	0.000	0.000	-0.500
Li	-0.500	-0.500	0.000
Li	0.000	-0.500	0.500
V	0.328	0.250	-0.278
V	-0.328	-0.250	0.278
V	0.172	-0.250	0.222
V	-0.172	0.250	-0.222
P	-0.374	0.250	0.372
P	0.374	-0.250	-0.372
P	-0.126	-0.250	-0.128
P	0.126	0.250	0.128
O	0.453	0.250	0.489
O	-0.453	-0.250	-0.489
O	0.047	-0.250	-0.011
O	-0.047	0.250	0.011
O	0.371	-0.055	-0.241
O	-0.371	0.055	0.241
O	0.129	0.055	0.259
O	-0.129	-0.055	-0.259
O	-0.371	0.445	0.241
O	0.371	-0.445	-0.241
O	-0.129	-0.445	-0.259
O	0.129	0.445	0.259
O	0.300	0.250	0.004
O	-0.300	-0.250	-0.004
O	0.200	-0.250	-0.496
O	-0.200	0.250	0.496

O	0.116	0.250	-0.344
O	-0.116	-0.250	0.344
O	0.384	-0.250	0.156
O	-0.384	0.250	-0.156

Table SI. 2. Structure of $Li_{1.5}VOPO_4$ before optimisation. a=6.643 Å, b=7.864 Å, c=7.521 Å, α=90.53°, β=90.00° and γ=90.00°.

Atom	Fractional Coordinate		
	x	y	z
Li	-0.192	0.304	-0.064
Li	0.192	-0.316	0.064
Li	-0.251	-0.200	-0.433
Li	0.050	0.045	0.482
Li	0.493	0.494	0.000
Li	0.458	0.042	0.491
V	-0.254	-0.374	0.257
V	0.254	0.368	-0.265
V	0.253	-0.136	-0.236
V	-0.254	0.124	0.237
P	-0.252	-0.134	-0.118
P	0.251	-0.371	0.384
P	-0.250	0.371	-0.383
P	0.250	0.122	0.124
O	-0.259	-0.452	-0.490
O	-0.242	0.045	-0.008
O	0.239	-0.059	0.016
O	0.260	0.457	0.499
O	0.061	0.133	0.244
O	-0.426	0.364	-0.248

O	-0.055	0.368	-0.267
O	0.436	0.115	0.250
O	-0.435	-0.123	-0.249
O	0.056	-0.373	0.269
O	-0.063	-0.142	-0.240
O	0.428	-0.372	0.249
O	-0.265	0.365	0.170
O	-0.248	-0.110	0.336
O	0.267	-0.399	-0.162
O	0.250	0.124	-0.328
O	0.259	-0.190	0.495
O	-0.257	0.195	-0.499
O	-0.270	-0.307	-0.005
O	0.267	0.292	0.005

Table SI.3. Structure of $Li_{1.5}VOPO_4$ after structural optimisation with PBE0 functional. a=6.402 Å, b=7.059 Å, c=7.534 Å, α=89.99°, β=89.36° and γ=89.99°.

Atom	Fractional Coordinate		
	x	y	z
Li	-0.109	0.313	-0.047
Li	0.134	-0.324	0.046
Li	-0.365	-0.189	-0.454
Li	-0.007	0.088	-0.439
Li	0.494	0.399	0.059
Li	0.388	0.180	0.452
V	-0.233	-0.380	0.255
V	0.254	0.370	-0.260
V	0.267	-0.134	-0.245
V	-0.247	0.116	0.240

P	-0.215	-0.132	-0.122
P	0.285	-0.382	0.378
P	-0.272	0.373	-0.378
P	0.228	0.113	0.122
O	-0.275	-0.443	-0.484
O	-0.208	0.054	-0.012
O	0.225	-0.071	0.016
O	0.293	0.432	0.487
O	0.065	0.114	0.276
O	-0.435	0.372	-0.224
O	-0.059	0.339	-0.289
O	0.441	0.147	0.211
O	-0.426	-0.146	-0.216
O	0.074	-0.369	0.283
O	-0.050	-0.118	-0.275
O	0.450	-0.396	0.225
O	-0.234	0.363	0.172
O	-0.264	-0.113	0.320
O	0.235	-0.401	-0.180
O	0.266	0.123	-0.329
O	0.329	-0.209	0.495
O	-0.305	0.198	-0.499
O	-0.170	-0.305	-0.006
O	0.196	0.289	0.001

Table SI. 4. Lowest energy structure of Li_2VOPO_4 (structure 1) after structural optimisation with PBE0 functional. a=6.394 Å, b=7.583 Å, c=7.220 Å, α=90.00°, β=89.99° and γ=90.00°.

Atom	Fractional Coordinate		

	x	y	z
Li	0.000	0.500	0.000
Li	0.500	0.000	-0.500
Li	-0.500	-0.500	0.000
Li	0.000	0.000	-0.500
Li	-0.250	-0.432	-0.225
Li	-0.250	-0.068	0.275
Li	0.250	0.432	0.225
Li	0.250	0.068	-0.275
V	0.250	-0.246	-0.129
V	0.250	-0.254	0.371
V	-0.250	0.246	0.129
V	-0.250	0.254	-0.371
P	0.250	0.126	0.131
P	0.250	0.374	-0.369
P	-0.250	-0.126	-0.131
P	-0.250	-0.374	0.369
O	0.250	0.010	-0.039
O	0.250	0.490	0.460
O	-0.250	-0.010	0.039
O	-0.250	-0.490	-0.460
O	-0.064	-0.259	-0.132
O	-0.436	-0.241	0.368
O	0.436	0.259	0.132
O	0.064	0.241	-0.368
O	0.064	0.259	0.132
O	0.436	0.241	-0.368
O	-0.436	-0.259	-0.132
O	-0.064	-0.241	0.368
O	0.250	0.485	-0.192
O	0.250	0.015	0.308

O	-0.250	-0.485	0.192
O	-0.250	-0.015	-0.308
O	0.250	-0.148	-0.381
O	0.250	-0.352	0.119
O	-0.250	0.148	0.381
O	-0.250	0.352	-0.119

Table SI. 5. Metastable structure of Li_2VOPO_4 (structure 2) after structural optimisation with PBE0 functional. a=6.521 Å, b=7.656 Å, c=7.310 Å, α=90.39°, β=90.00° and γ=90.00°.

Atom	Fractional Coordinate		
	x	y	z
Li	-0.269	-0.442	-0.064
Li	-0.478	-0.163	-0.384
Li	0.231	0.442	0.064
Li	0.022	0.163	0.384
Li	-0.271	-0.053	0.309
Li	0.229	0.053	-0.309
Li	0.494	0.316	0.372
Li	-0.006	-0.316	-0.372
V	0.251	-0.247	-0.113
V	0.248	-0.257	0.363
V	-0.249	0.247	0.114
V	-0.252	0.257	-0.363
P	0.252	0.118	0.122
P	0.246	0.378	-0.369
P	-0.248	-0.118	-0.122
P	-0.254	-0.378	0.370
O	0.253	0.013	-0.055
O	0.254	0.485	0.453
O	-0.247	-0.013	0.055
O	-0.246	-0.485	-0.453

O	-0.068	-0.251	-0.128
O	-0.437	-0.246	0.380
O	0.432	0.251	0.128
O	0.063	0.246	-0.380
O	0.064	0.244	0.136
O	0.431	0.251	-0.373
O	-0.436	-0.245	-0.136
O	-0.069	-0.252	0.373
O	0.228	0.492	-0.198
O	0.246	0.009	0.298
O	-0.272	-0.492	0.198
O	-0.254	-0.009	-0.298
O	0.242	-0.179	-0.376
O	0.252	-0.328	0.122
O	-0.257	0.179	0.376
O	-0.248	0.328	-0.122

Table SI. 6. Key Li-Li distances in Structure 2 of β-Li_2VOPO_4. (The structure is depicted in Fig. 2(e) of the main text).

Labels		Li-Li Distances (Å)
Li2	Li6	2.8
Li1	Li5	3.0
Li1	Li2	3.3
Li5	Li6	3.5