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Supporting Information

Understanding the structural phase transitions in lithium vanadium phosphate cathode for lithium-ion batteries

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Table S1. Atomic position (X, Y, Z), temperature factors (B), and occupancy of each element in $Li_3V_2(PO_4)_3$ calculated by Rietveld refinement.

*** : fixed**

Atom	X	Y	Z	B	Occ
Li1	0.206(7)	0.755(7)	0.168(5)	1*	1*
Li2	0.955(7)	0.303(7)	0.216(5)	1*	1*
Li3	0.556(7)	0.442(6)	0.189(4)	1*	1*
V1	0.2493(9)	0.4614(7)	0.1113(5)	1.5(1)	1*
V2	0.7525(9)	0.4692(7)	0.3902(5)	1.8(1)	1*
P1	0.105(1)	0.105(1)	0.1498(2)	1.6(2)	1*
P2	0.605(1)	0.116(1)	0.3513(8)	2.0(2)	1*
P3	0.038(1)	0.0249(1)	0.4925(9)	1.7(2)	1*
O1	0.924(2)	0.111(2)	0.146(1)	1.6(5)	1*
O2	0.140(2)	0.981(2)	0.233(1)	2.2(5)	1*
O3	0.189(2)	0.042(1)	0.041(1)	2.5(5)	1*
O4	0.162(2)	0.270(3)	0.184(1)	3.0(6)	1*
O5	0.429(2)	0.087(2)	0.339(1)	1.7(5)	1*
O6	0.686(2)	-0.004(2)	0.276(1)	2.5(6)	1*
O7	0.642(2)	0.093(2)	0.474(1)	3.2(6)	1*
O8	0.644(2)	0.278(2)	0.321(1)	1.4(5)	1*
O9	0.941(2)	0.129(2)	0.560(1)	1.2(4)	1*
O10	0.923(2	0.328(2)	0.403(1)	3.2(6)	1*
O11	0.163(2)	0.164(2)	0.432(1)	1.9(5)	1*
O12	0.112(2)	0.368(1)	0.574(1)	1.8(5)	1*

Figure S1. Illustration of $Li_3V_2(PO_4)_3$ unit cell structure.

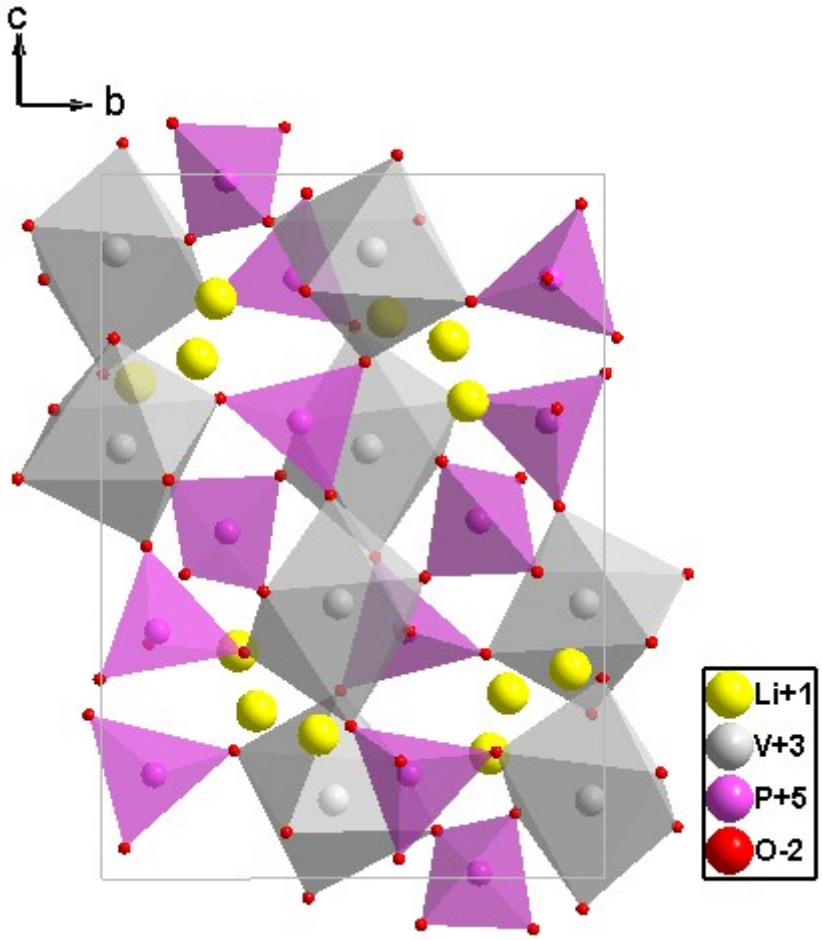


Figure S2. The first and second charge-discharge curves of LVP in the voltage ranges of 3.0 to 4.8V at C/5 rate.

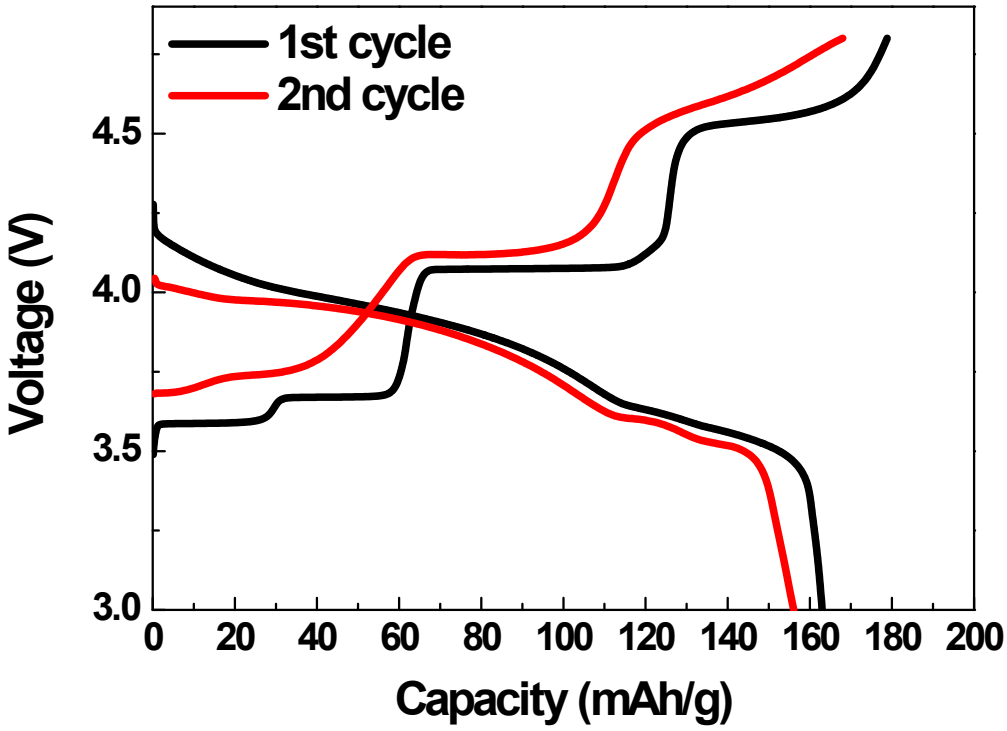


Figure S3. Lattice parameter (*a*, b, c) and unit cell volume (V) change during the first charge.

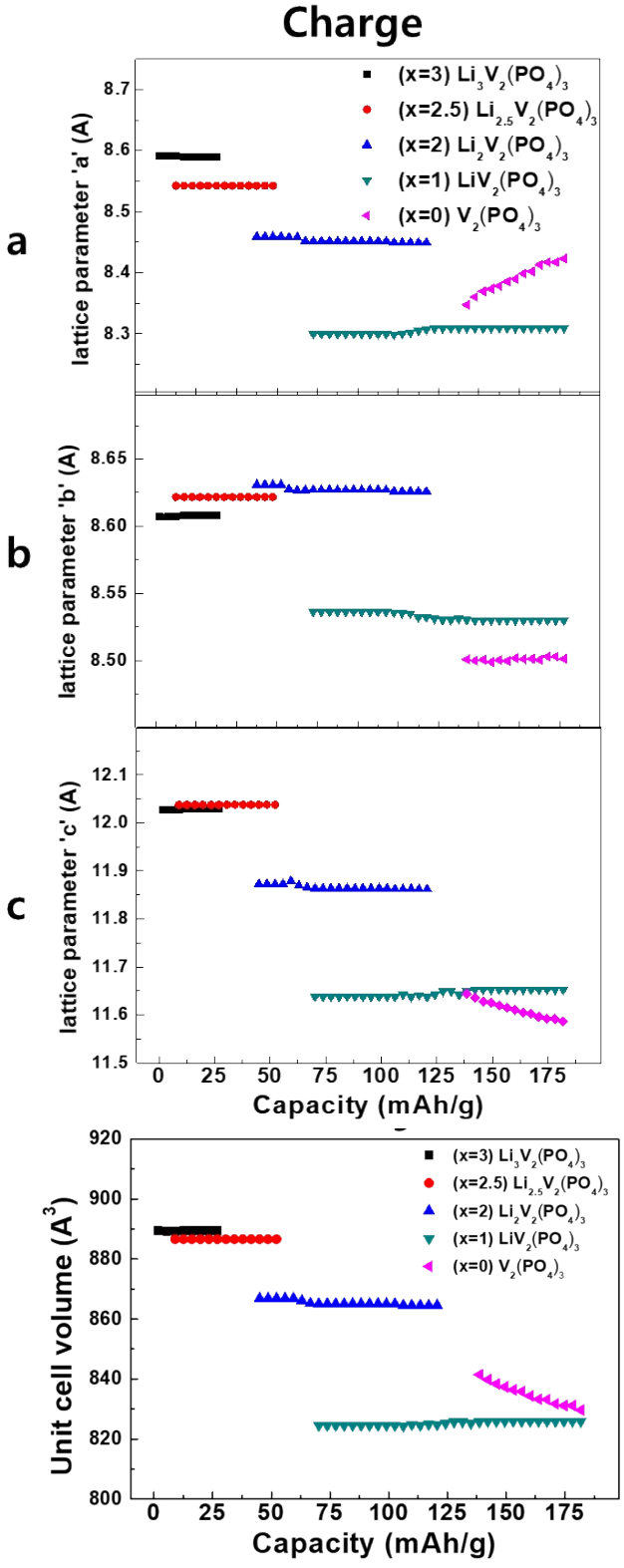


Figure S4. Illustration of oxygen ligand around the Li site during phase transition from $LiV_2(PO_4)_3$ to $Li_{1-x}V_2(PO_4)_3$.

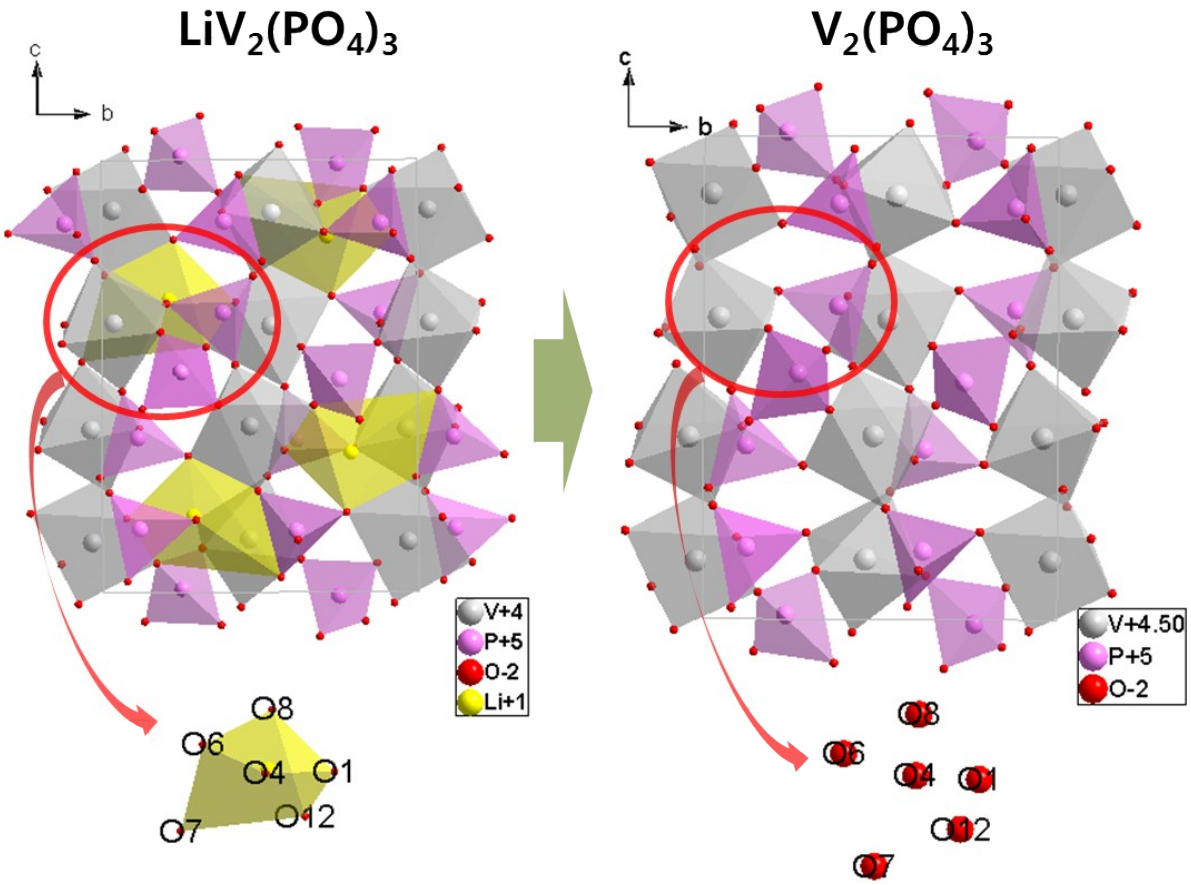


Table S2. O-O distance of Li site in $LiV_2(PO_4)_3$ and $V_2(PO_4)_3$ phase, and the difference.

LiV2(PO4)3		V2(PO4)3		Difference
O8-O6	2.570Å	O8-O6	2.790Å	0.220Å
O8-O4	4.029Å	O8-O4	4.763Å	0.734Å
O8-O1	3.151Å	O8-O1	3.191Å	0.040Å
O8-O12	3.290Å	O8-O12	3.219Å	-0.071Å
O8-O7	4.238Å	O8-O7	5.639Å	1.401Å
O6-O4	2.834Å	O6-O4	3.006Å	0.172Å
O6-O1	3.665Å	O6-O1	3.672Å	0.007Å
O6-O12	4.372Å	O6-O12	4.005Å	-0.367Å
O6-O7	2.453Å	O6-O7	2.489Å	0.036Å
O1-O12	3.686Å	O1-O12	2.549Å	-1.137Å
O1-O7	4.570Å	O1-O7	4.571Å	0.001Å
O1-O4	2.434Å	O1-O4	2.422Å	-0.012Å
O12-O7	4.107Å	O12-O7	3.751Å	-0.356Å
O12-O4	5.195Å	O12-O4	4.290Å	-0.905Å
O7-O4	3.797Å	O7-O4	4.167Å	0.370Å

Tables S3. O-P-O bond angle, and P-O distance of Li site in $LiV_2(PO_4)_3$ and $V_2(PO_4)_3$ phase, and the difference.

Angle				
LiV2(PO4)3		V2(PO4)3		Difference
O1-P1-O2	107.54	O1-P1-O2	113.37	5.83
O1-P1-O3	110.52	O1-P1-O3	112.63	2.11
O1-P1-O4	103.92	O1-P1-O4	104.72	0.8
O2-P1-O3	110.53	O2-P1-O3	108.05	-2.48
O2-P1-O4	113.12	O2-P1-O4	104.44	-8.68
O3-P1-O4	110.96	O3-P1-O4	113.42	2.46
O5-P2-O6	110.42	O5-P2-O6	114.69	4.27
O5-P2-O7	111.85	O5-P2-O7	106.37	-5.48
O5-P2-O8	112.19	O5-P2-O8	116.84	4.65
O6-P2-O7	106.57	O6-P2-O7	107.4	0.83
O6-P2-O8	107.1	O6-P2-O8	105.8	-1.3
O7-P2-O8	108.44	O7-P2-O8	105	-3.44
O9-P3-O10	109.07	O9-P3-O10	107.79	-1.28
O9-P3-O11	115.26	O9-P3-O11	106.9	-8.36
O9-P3-O12	70.97	O9-P3-O12	112.41	41.44
O10-P3-O11	104.29	O10-P3-O11	96.67	-7.62
O10-P3-O12	82.32	O10-P3-O12	118.67	36.35
O11-P3-O12	167.84	O11-P3-O12	112.86	-54.98

Distance				
LiV2(PO4)3		V2(PO4)3		Difference
P1-O1	1.551	P1-O1	1.557	0.006
P1-O2	1.546	P1-O2	1.589	0.043
P1-O3	1.490	P1-O3	1.553	0.063
P1-O4	1.540	P1-O4	1.502	-0.038
P2-O5	1.527	P2-O5	1.434	-0.093
P2-O6	1.521	P2-O6	1.405	-0.116
P2-O7	1.539	P2-O7	1.677	0.138
P2-O8	1.540	P2-O8	1.524	-0.016
P3-O9	1.528	P3-O9	1.536	0.008
P3-O10	1.559	P3-O10	1.486	-0.073
P3-O11	1.511	P3-O11	1.697	0.186
P3-O12	0.988	P3-O12	1.424	0.436

Figure S5. Lattice parameter (*α*, b, c) and unit cell volume (V) change during the first discharge.

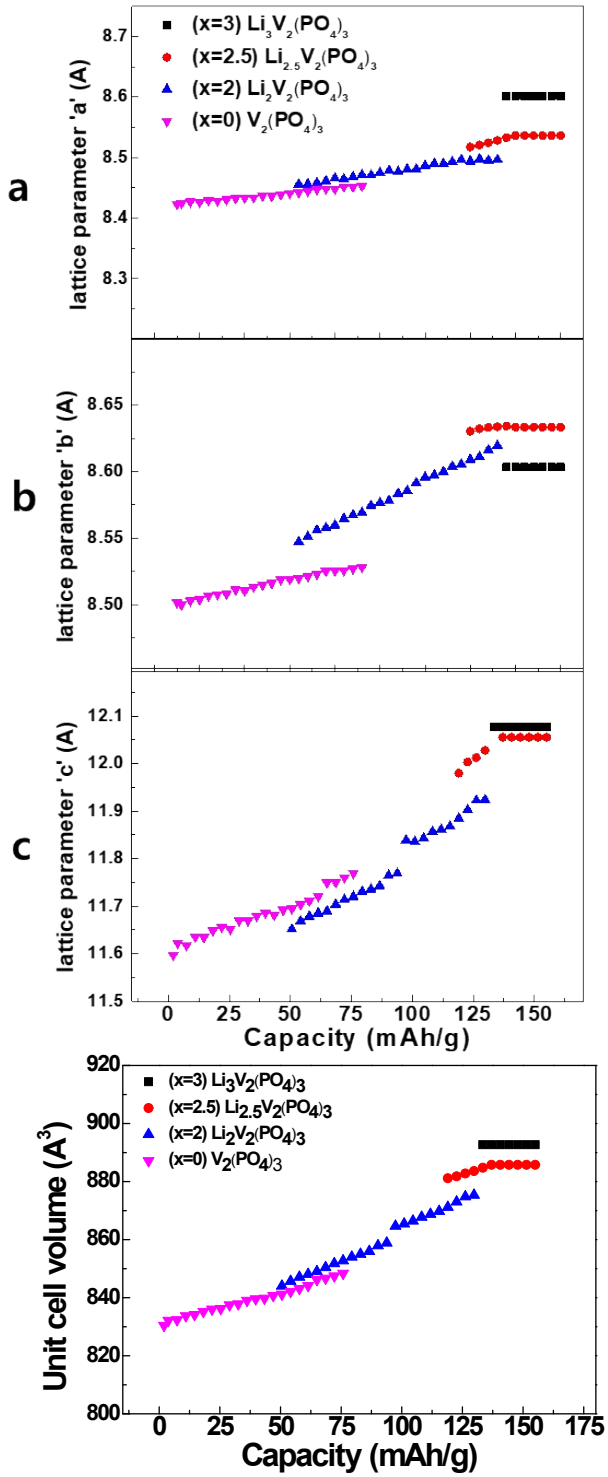


Figure S6. Vanadium K-edge X-ray absorption spectrums of $Li_3V_2(PO_4)_3$ during the charge process (a) points of each sample, (b) overall spectrums, and (c) pre-edge area.

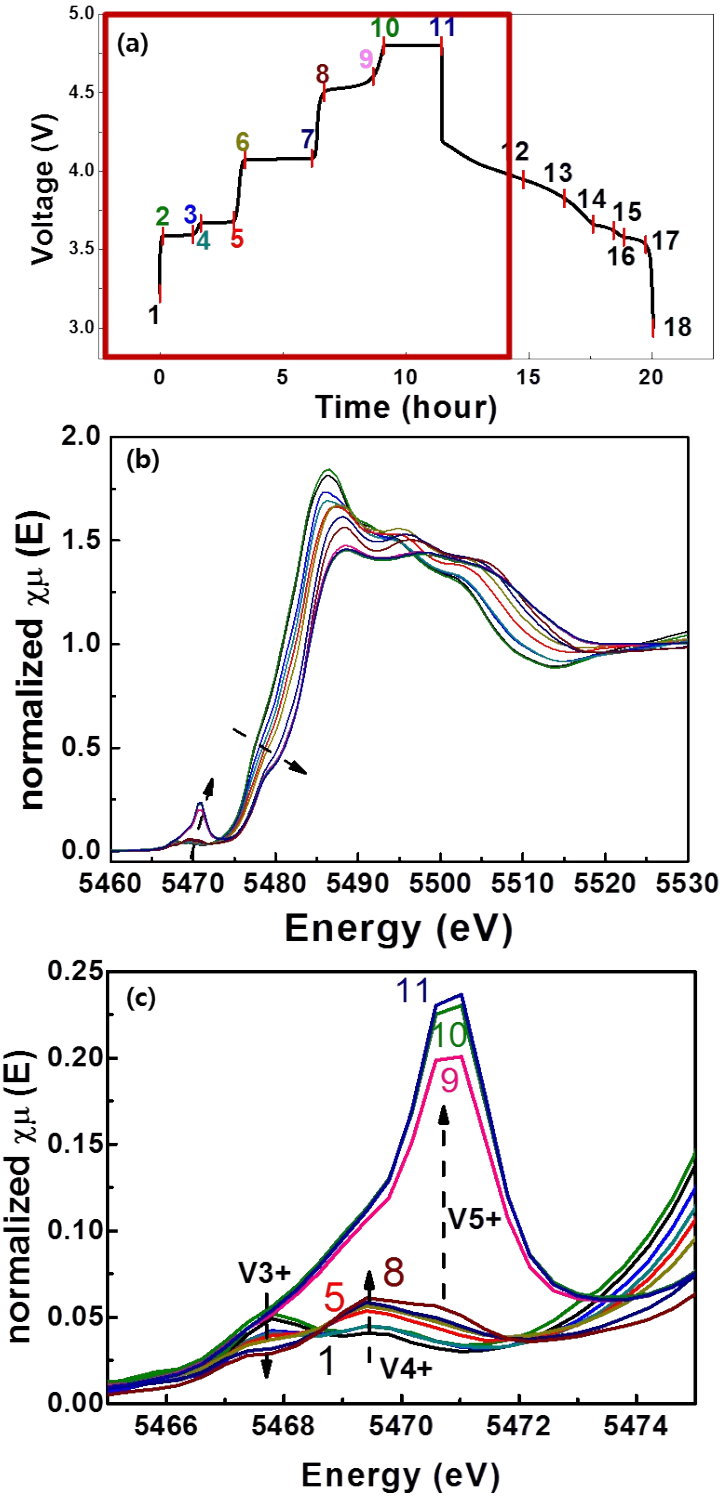


Figure S7. Vanadium K-edge X-ray absorption spectrums of $Li_3V_2(PO_4)_3$ during the discharge process (a) points of each sample, (b) overall spectrums and (c) pre-edge area.

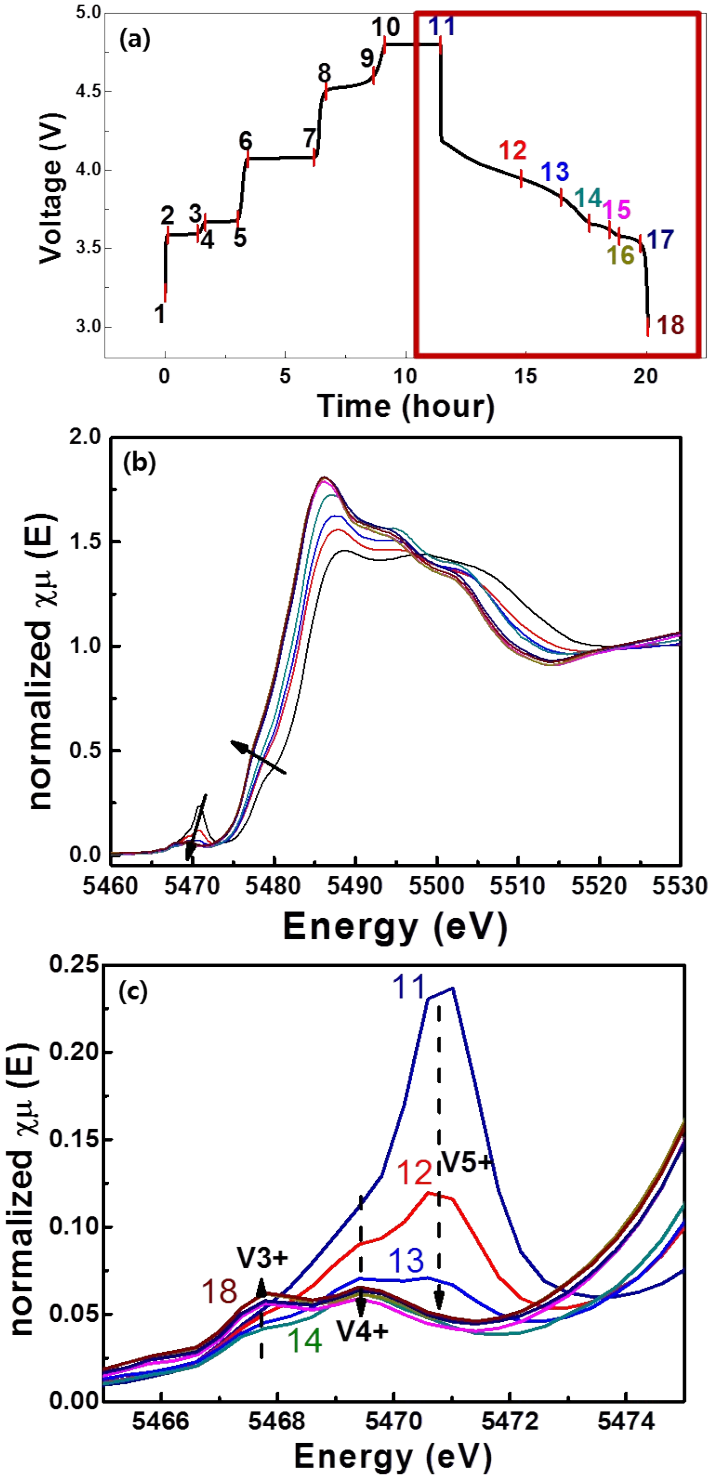
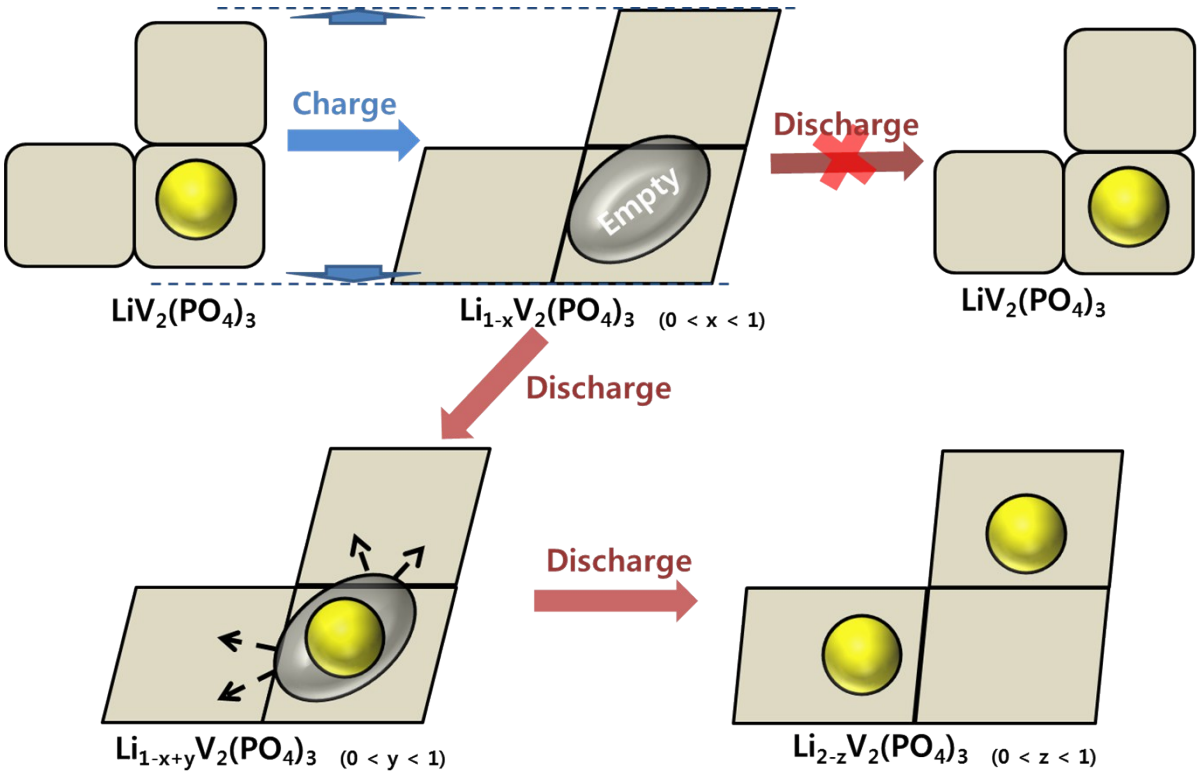


Figure S8. Schematic illustration of Li-site transition at the end of the charge and at the beginning of the discharge.

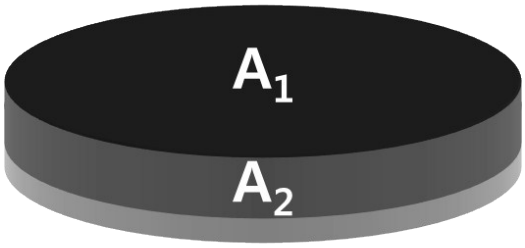


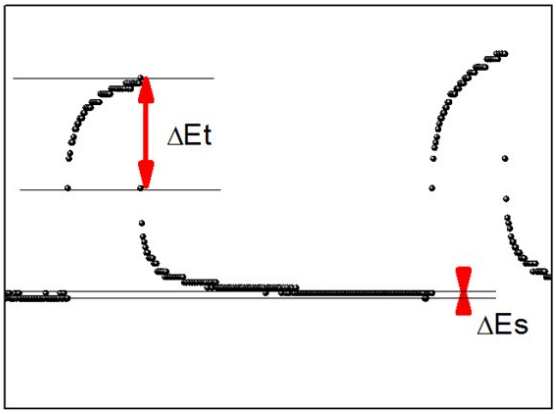
$Li_1V_2(PO_4)_3 + xe^- \rightarrow Li_{1-x}V_2(PO_4)_3 + xLi^+$ (0 <x<1)

$Li_{1-x}V_2(PO_4)_3 + yLi^+ \rightarrow Li_{1-x+y}V_2(PO_4)_3 + ye^-$ (0 < y < 1)

(when x ≈ y), $Li_{1-x+y}V_2(PO_4)_3 \rightarrow Li_{2-z}V_2(PO_4)_3$(0 < z < 1)

Figure S9. Schematic illustration of LVP/G electrode used for calculating lithium diffusion coefficient.





$$D_{Li+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B A}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \left(\tau \ll L^2/D_{Li+}\right)$$

-Applied current :C/20

-Rest time : 40min

-Current applying time(τ) : 10 min = 600 s

-Mess of active material in the electrode (m_B) : 0.00134 g

-Volume of the electrode (V_M) : [(0.7 x 0.7 x π) x (0.002)] cm^3 = 3.077e-3 cm^3

-Molar weight of $Li_3V_2(PO)_3$(M_B): 407.62 g mol-1

-Surface area of electrode (A) : A1+A2 =[(0.7 x 0.7 x π)+(1.4 π x 0.002)]cm^2 = 1.54739 cm^2