Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary information

A square channel vanadium phosphite framework as high voltage cathode for Li- and Na- ion batteries

*Prashanth Sandineni[a], Pranal Madria[a], Kartik Ghosh[b], and Amitava Choudhury[a,]**

[a]Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, USA.

[b]Department of Physics, Astronomy and Materials Science and Center for Applied Science and Engineering, Missouri State University, Springfield, Missouri 65897, USA.

*Corresponding author, e-mail: choudhurya@mst.edu

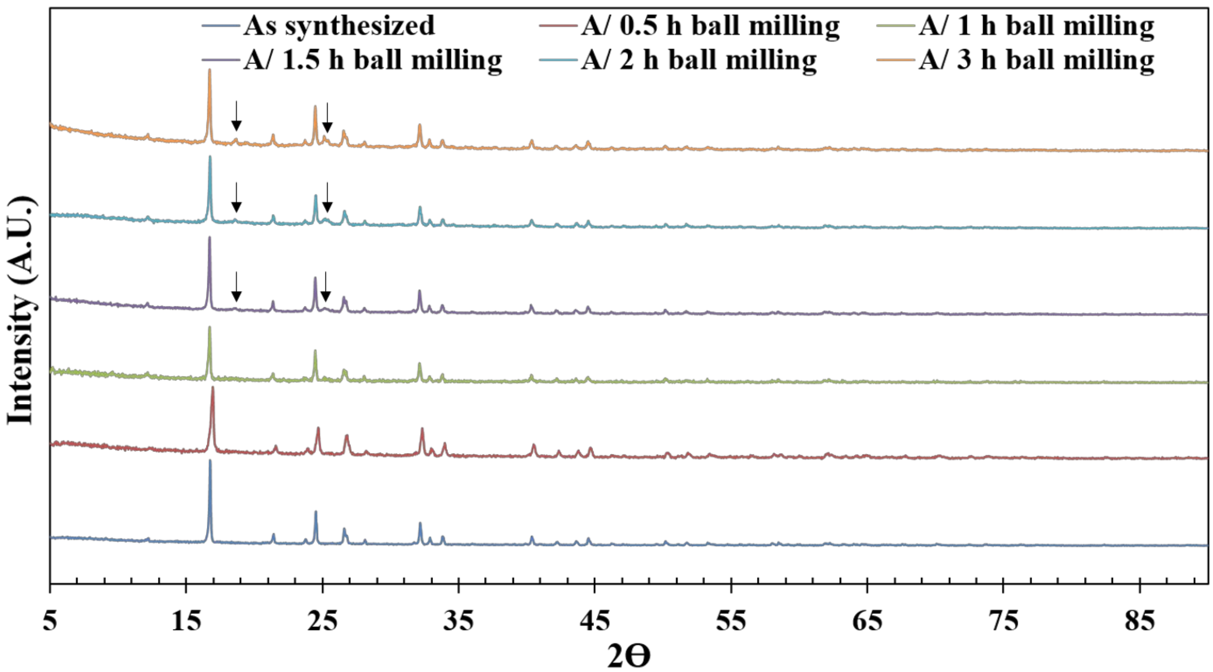

Figure S1. Comparison of PXRD data of ball milled samples with as synthesized $LiV(HPO_3)_2$.

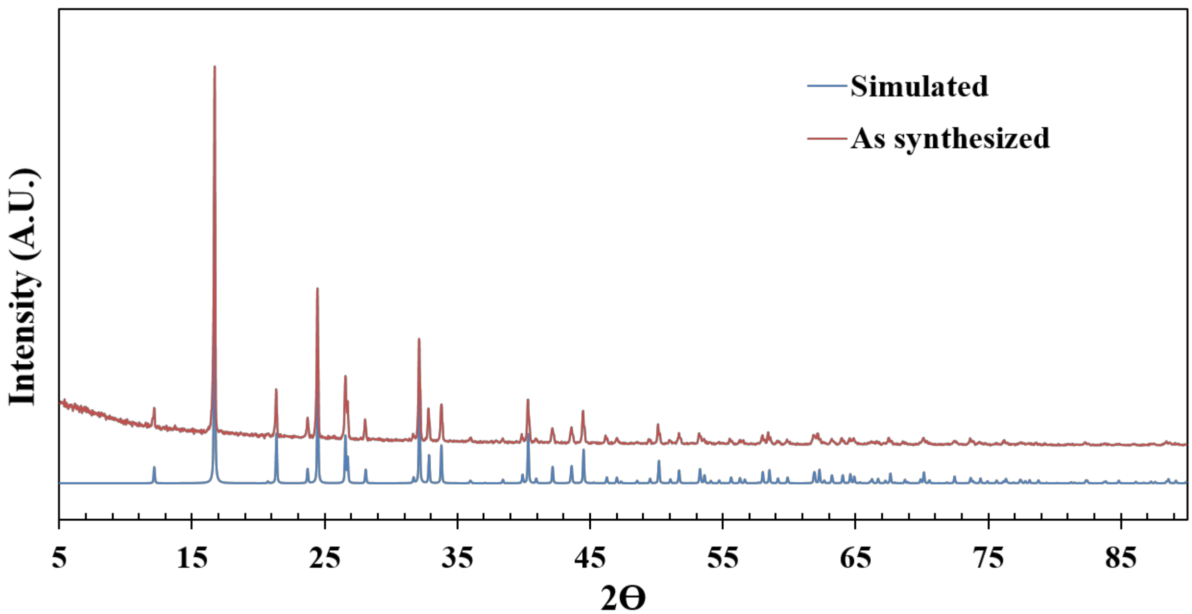

Figure S2. Comparison of PXRD data of as synthesized $LiV(HPO_3)_2$ with simulated.

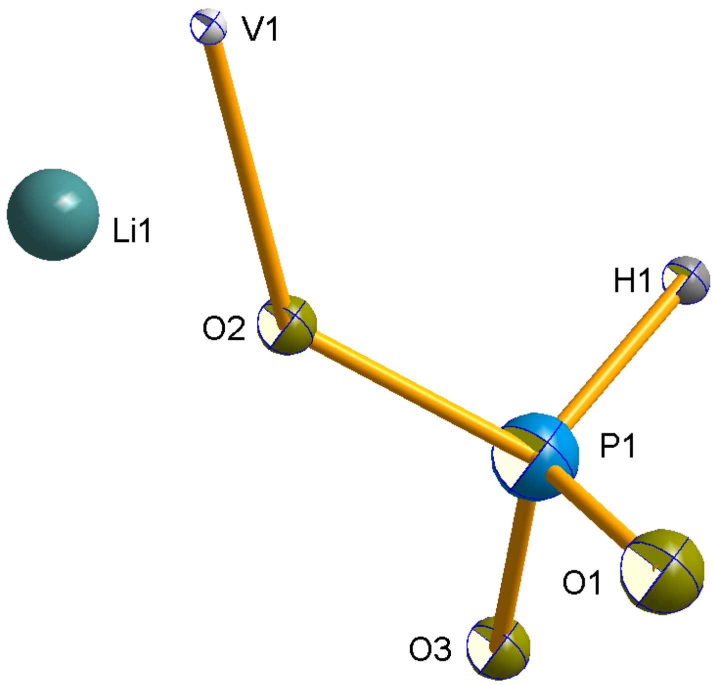

Figure S3. Asymmetric unit of $LiV(HPO_3)_2$.

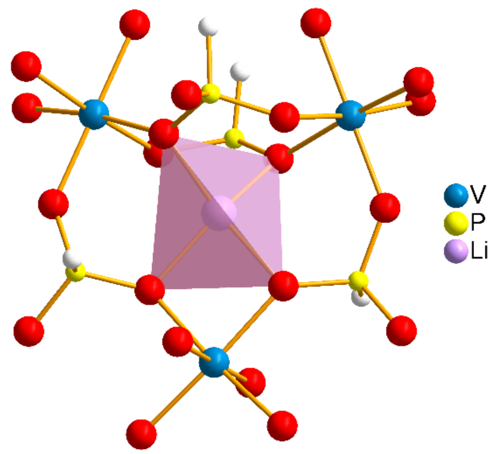

Figure S4. Li-coordination in $LiV(HPO_3)_2$.

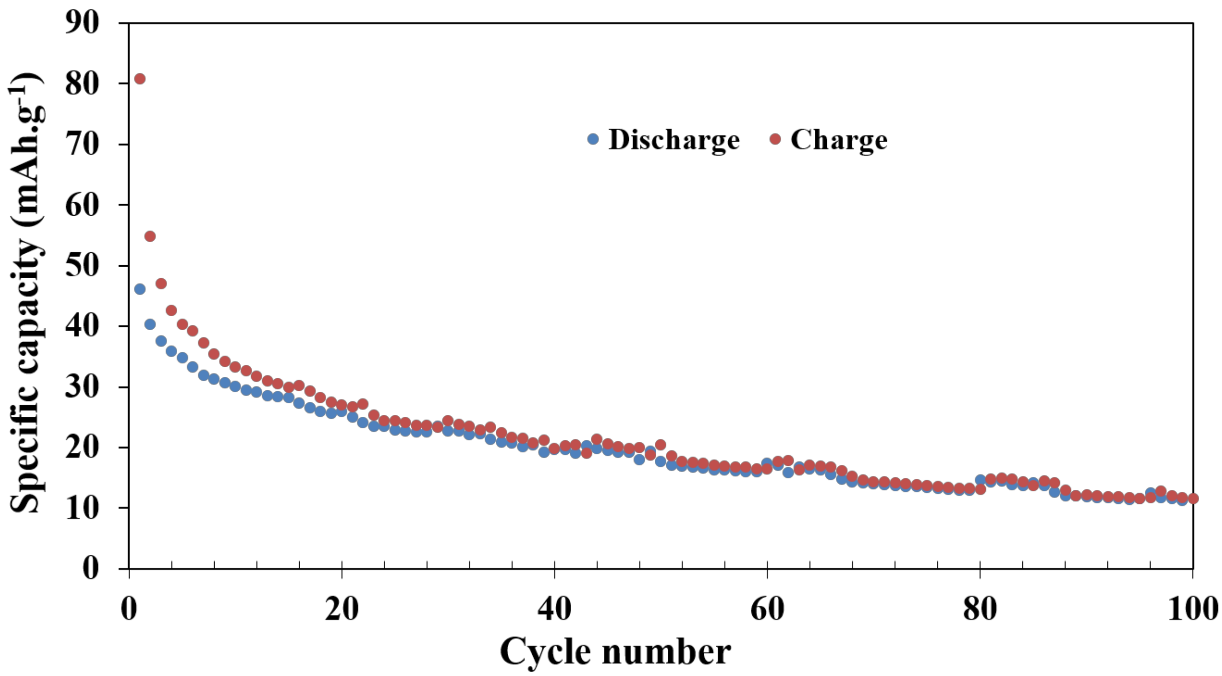

Figure S5. Cycle index of Li-ion battery at C/5 rate for 100 cycles. (from 1.2 V to 4.5 V).

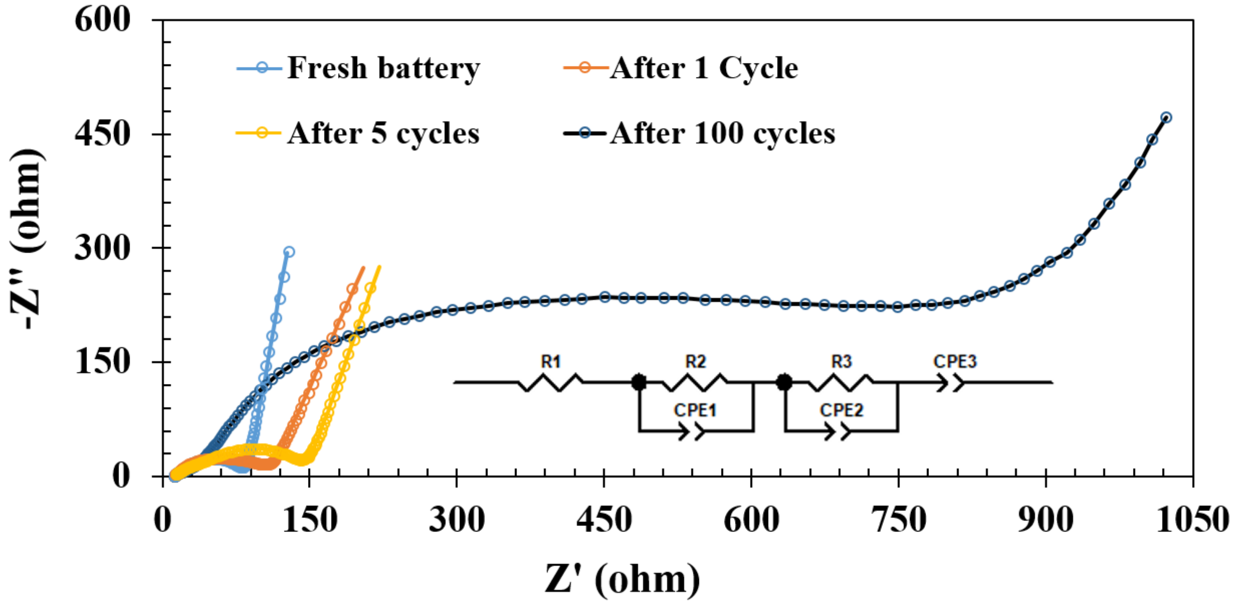

Figure S6. Nyquist plots of freshly fabricated and cycled Li-ion batteries.

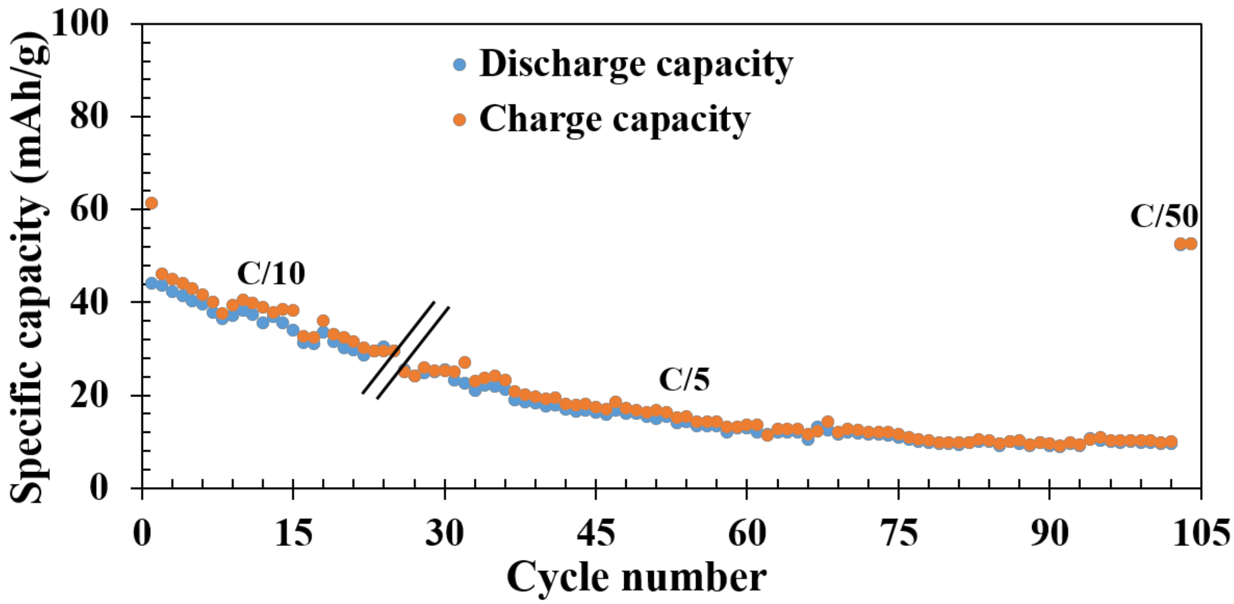

Figure S7. Cycle index of Na-ion battery at C/10 and C/5 rate for 100 cycles.

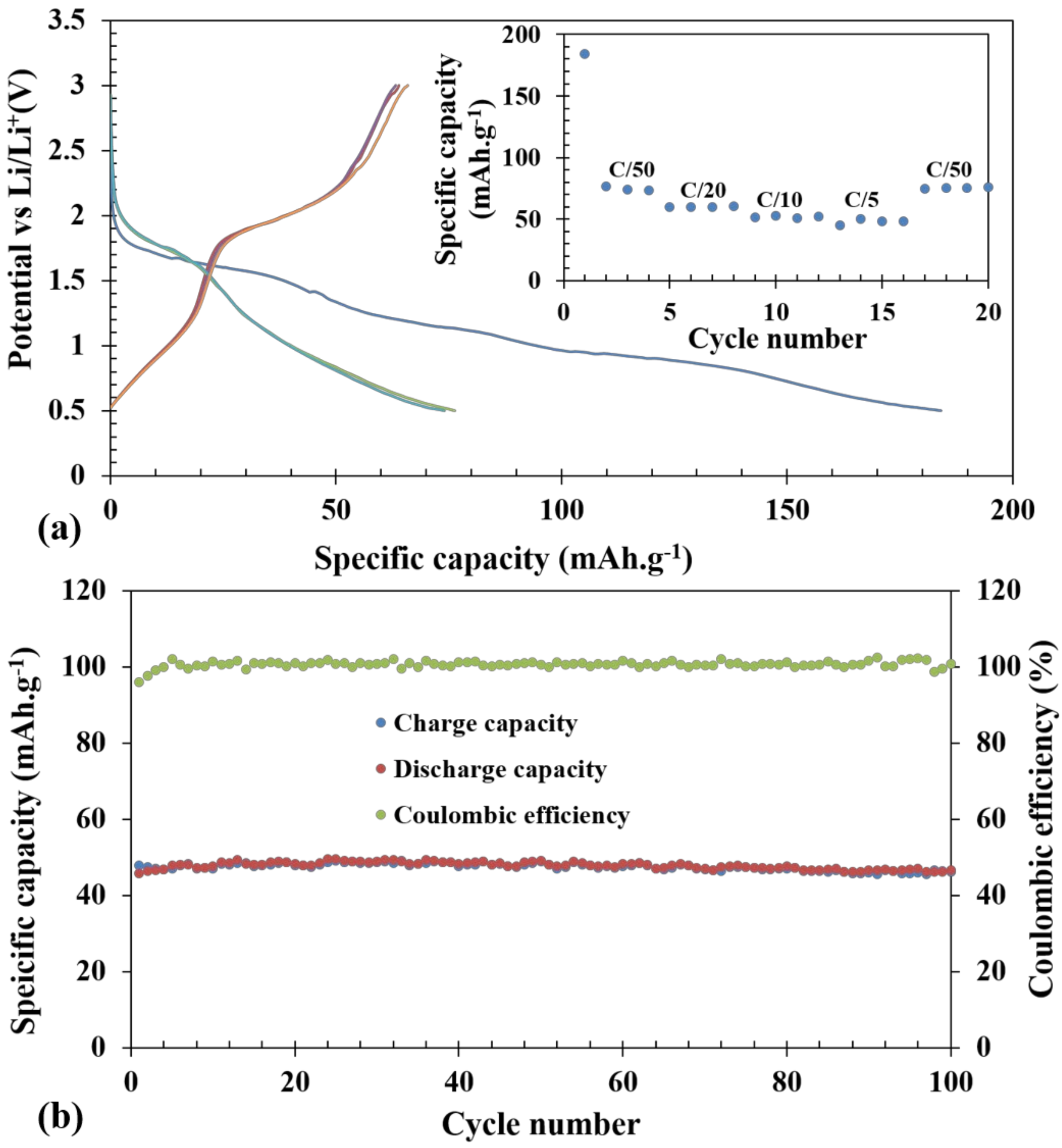

Figure S8. Galvanostatic charge-discharge profiles for Li-ion batteries from 0.5 V to 3.0 V at C/50 (a). (Inset shows discharge specific capacity at different C-rates). Cycle index of Li-ion battery along with coulombic efficiency at C/5 rate for 100 cycles after initial 20 cycles at different C-rates (b).

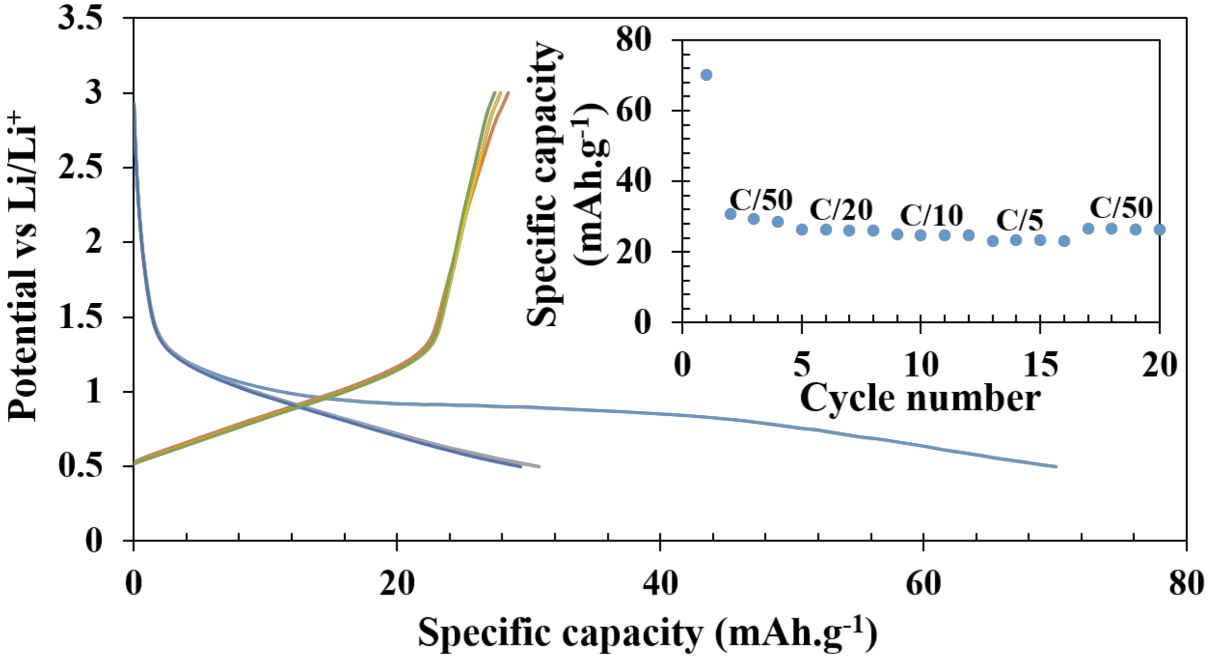

Figure S9. Galvanostatic charge-discharge profiles for half cell with lithium anode and super P carbon as cathode at C/50 from 0.5 V to 3.0 V. (Inset shows discharge specific capacity at different C-rates).

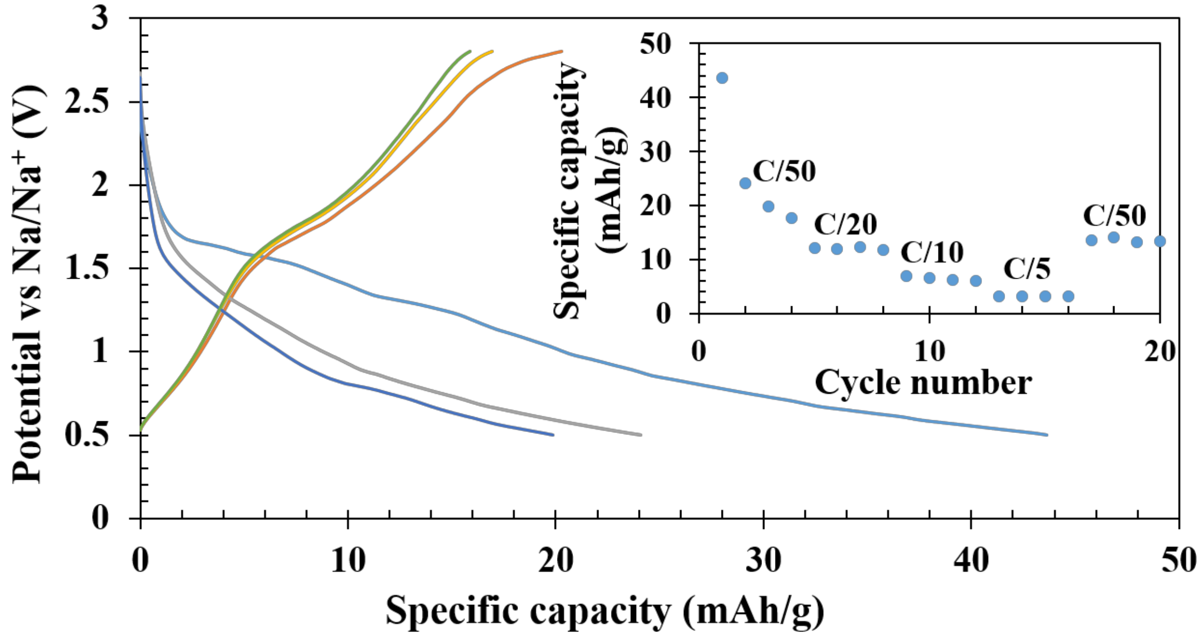

Figure S10. Galvanostatic charge-discharge profiles for Na-ion batteries at C/50 from 0.5 V to 2.8 V. (Inset shows discharge specific capacity at different C-rates).

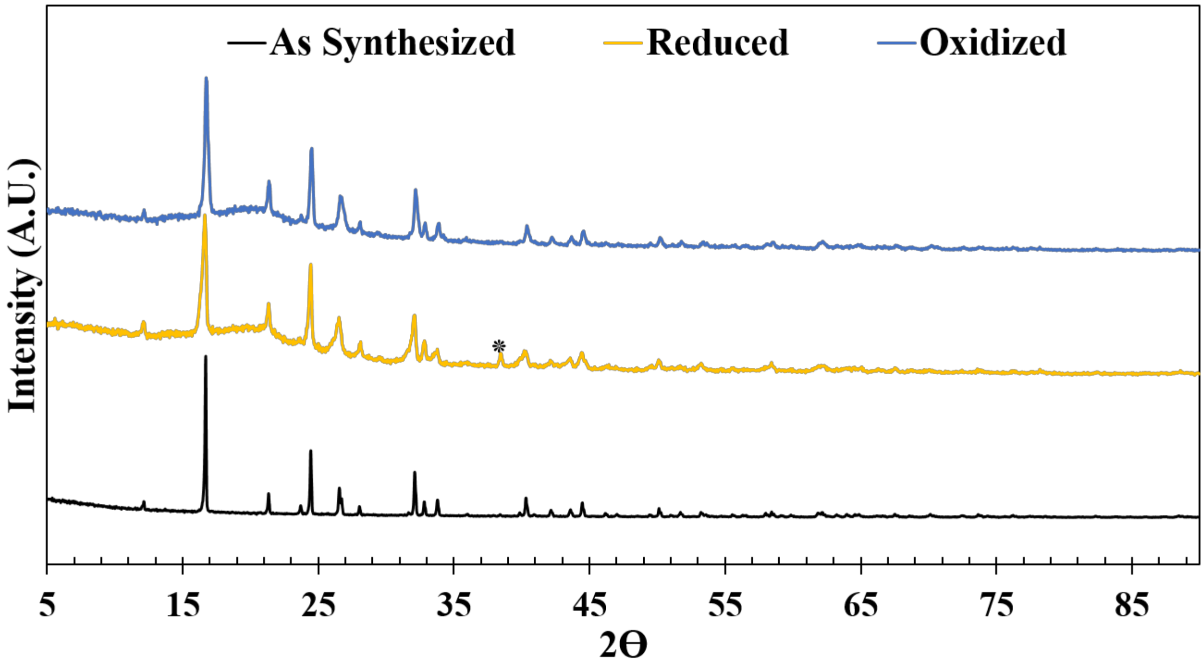

Figure S11. Comparison of PXRDs of oxidized and reduced (chemically) samples with as-synthesized pristine, $LiV(HPO_3)_2$. (* indicates Al peak)

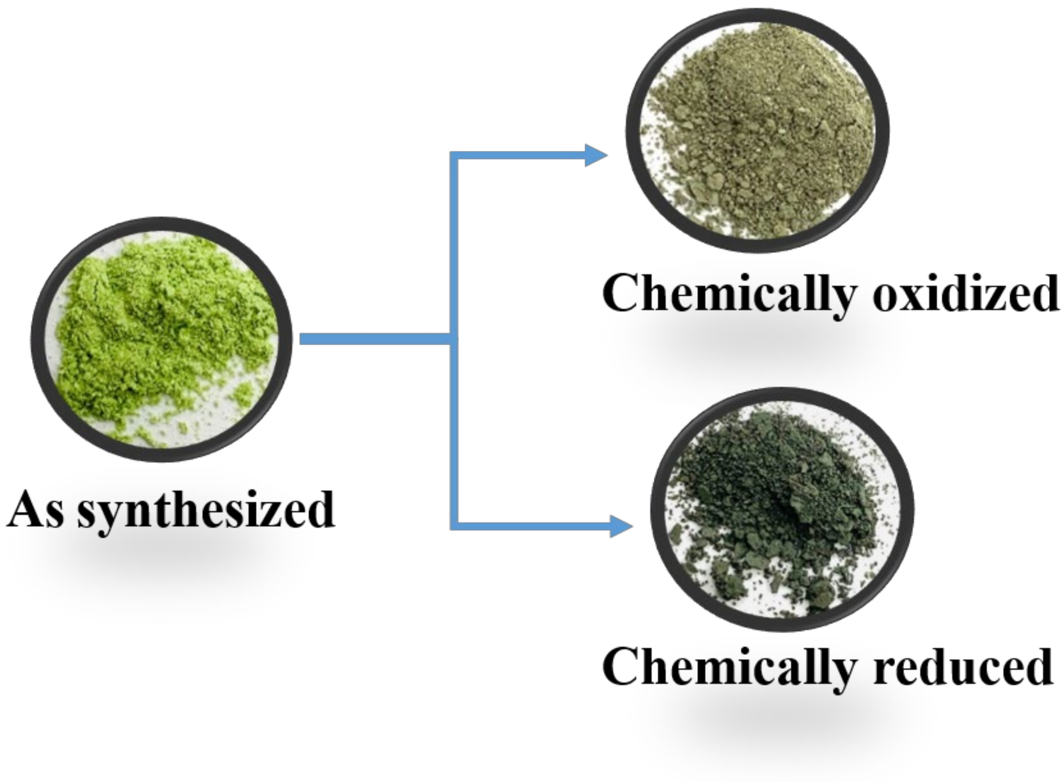

Figure S12. A photograph of the as-synthesized, chemically reduced and chemically oxidized $LiV(HPO_3)_2$.

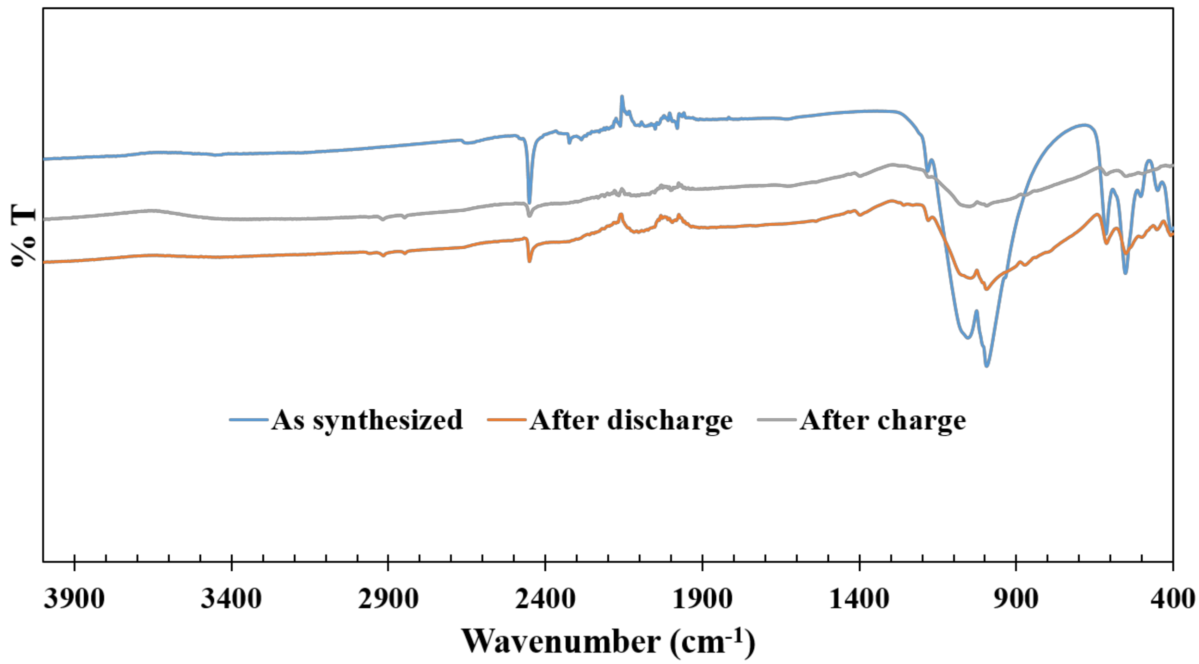

Figure S13. FT-IR spectra of cathode materials (after charge & discharge) in comparison with as synthesized sample of $LiV(HPO_3)_2$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of $LiV(HPO_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	Wyckoff	x/a	y/b	z/c	U(eq)
V(1)	8d	0.2843(3)	0.2500(3)	0.1250(3)	0.004(1)
P(1)	16e	0.4463(3)	0.2479(8)	0.4011(8)	0.015(1)
O(1)	16e	0.3431(7)	0.1911(8)	0.4882(9)	0.014(1)
O(2)	16e	0.4244(9)	0.2126(2)	0.2548(9)	0.007(1)
O(3)	16*e*	0.5787(2)	0.2154(8)	0.4485(9)	0.008(1)
Li(1)	8d	0.5651(3)	0.2500(3)	0.1250(3)	0.025(1)
H(1)	16e	0.4440(8)	0.3736(8)	0.4090(8)	0.007(1)

Table S2. Impedance equivalent circuit parameters for freshly fabricated and cycled cells.

				CPE1		CPE2		CPE3	
	R_s (Ω)	R_{SEI} (Ω)	R_{Ct} (Ω)	C (μF)	P	C (μF)	P	C (μF)	P
Fresh battery	12.56		74.94			75.07	0.65	2246	0.91
After 1 cycle	12.41	11.41	86.45	217	0.91	35.93	0.63	2688	0.78
After 5 cycles	9.59	65.17	72.98	156	0.48	52.01	0.80	2707	0.83
After 100 cycles	11.64	660.6	67.97	51	0.67	99.19	0.31	1695	0.49

Table S3. Rietveld refinement values of cathode materials at different states of discharge. 1, 2, 3, 4 and 5 refers to the position in the discharge curve in the Figure 8a where cells were broken.

Cell parameters	1	2	3	4	5
a = *b* (Å)	10.579(5)	10.618(4)	10.627(4)	10.658(3)	10.768(2)
c (Å)	9.990(3)	10.010(2)	10.014(5)	10.060(3)	10.085(3)
V (Å3)	1118.18(5)	1128.76(4)	1131.08(5)	1142.84(5)	1169.39(3)
w*R*	12.45 %	10.37 %	12.07 %	11.07 %	12.71 %

Table S4. Rietveld refinement values of oxidized and reduced (chemically & electrochemically) samples in comparison with as synthesized sample of $LiV(HPO_3)_2$.

Cell parameters	As synthesized	Chemically Oxidized	Chemically Reduced
$a = b$ (Å)	10.5987(4)	10.589 (3)	10.651(2)
c (Å)	9.9843(5)	9.996 (3)	9.979(3)
V (Å3)	1121.57(4)	1120.99(5)	1132.23(3)
wR	12.45 %	8.78 %	11.07 %