Supporting information

Ammonium Vanadium Bronze, $(NH_4)_2V_7O_{16}$, as a New Lithium Intercalation Host Material

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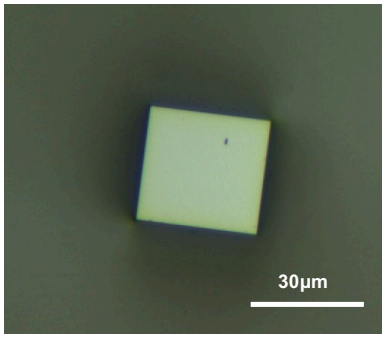

Figure S1. A thin plate-shaped single-crystal image of $(NH_4)_2V_7O_{16}$.

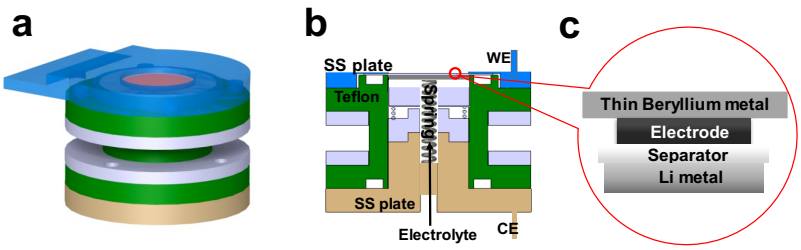

Figure S2. In-situ XRD cell. (a) side view, (b) section view, and (c) magnified view of the electrode section.

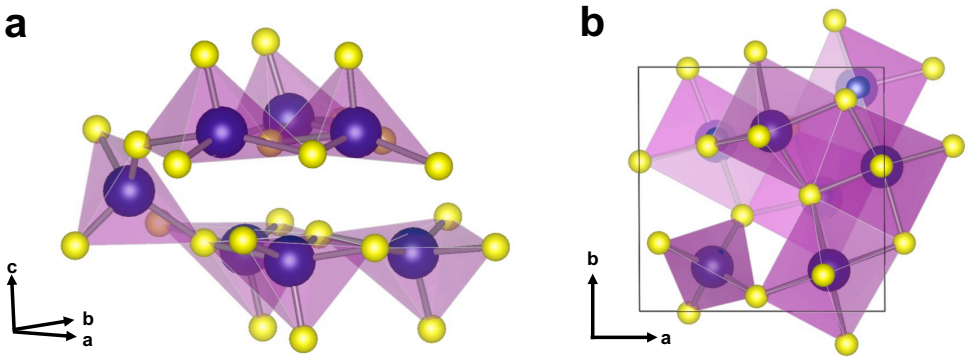

Figure S3. (a) Basic motif of V_7O_{16} layer, composed of six VO_5 pyramids and one VO_4 tetrahedron. (b) (001) view of the motif.

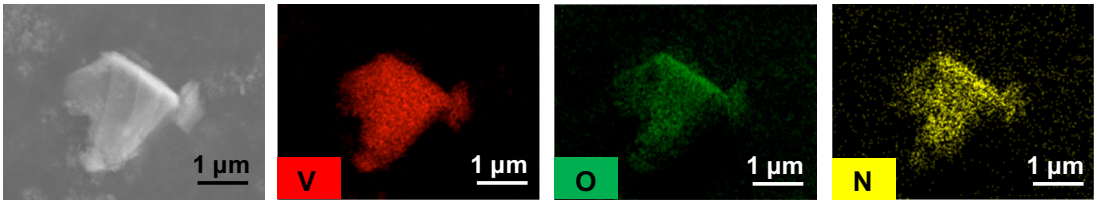

Figure S4. HR FE-SEM EDX elemental mappings of $(NH_4)_2V_7O_{16}$ electrode. Note that V, O and N atoms are well distributed over the particles.

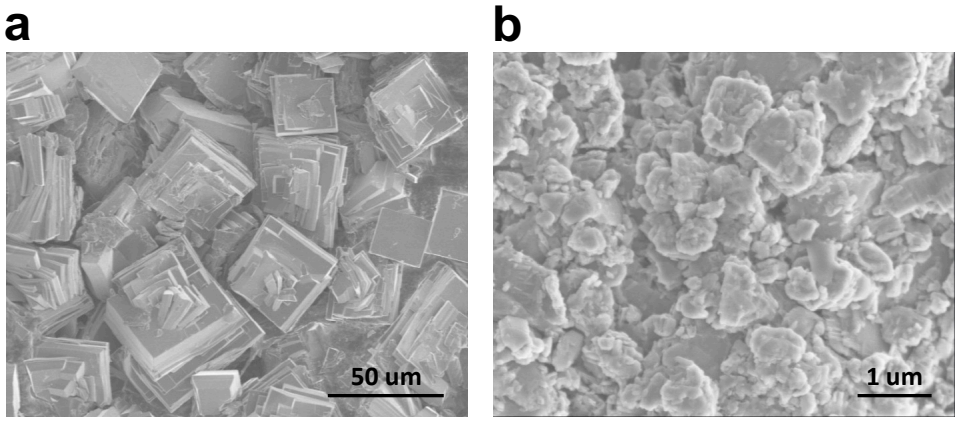

Figure S5. SEM images of (a) as-synthesized and (b) ball-milled $(NH_4)_2V_7O_{16}$ powder.

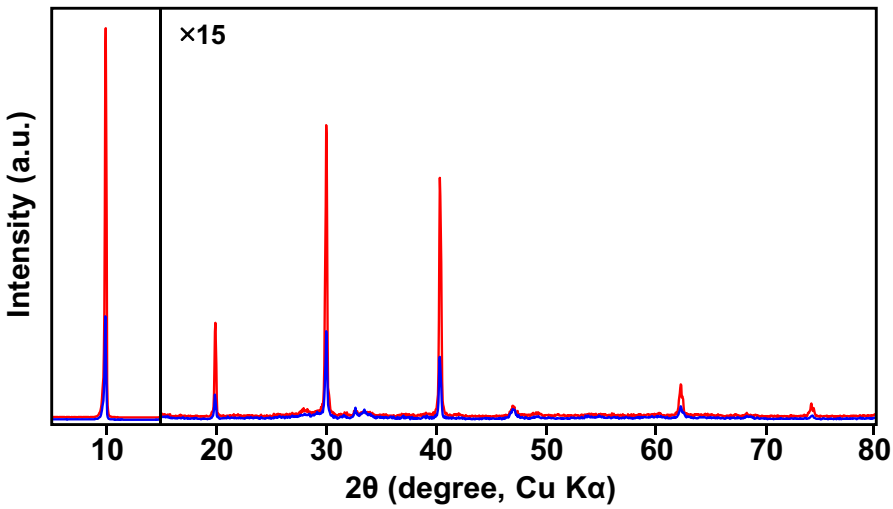

Figure S6. Powder XRD pattern of (red) as-synthesized and (blue) ball-milled $(NH_4)_2V_7O_{16}$.

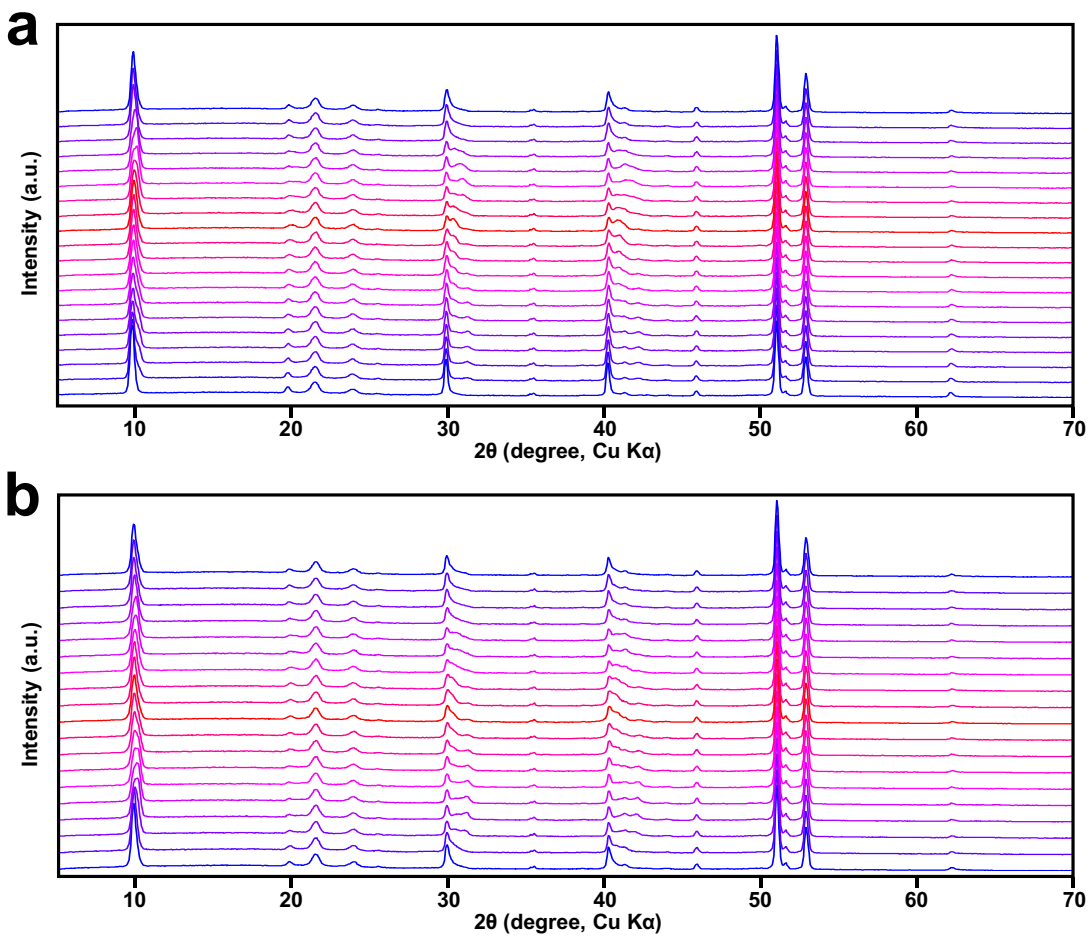

Figure S7. Evolution of the in situ XRD patterns for the $(NH_4)_2V_7O_{16}$ composite electrodes during (a) the first and (b) the second discharge/charge cycle.

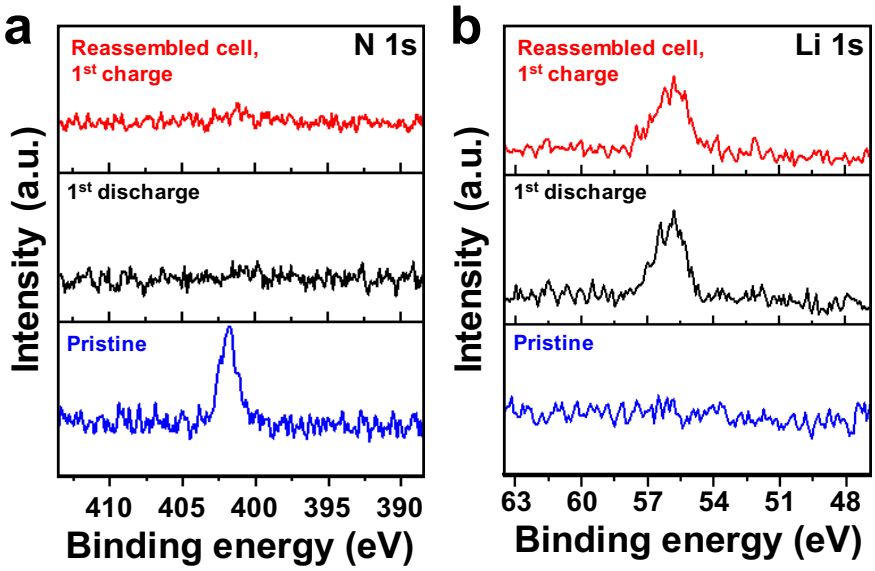

Figure S8. XPS results for $(NH_4)_2V_7O_{16}$ electrodes at three different states. (a) N 1s spectrum and (b) Li 1s spectrum. The reassembled cell showed Li clearly even at the charged state.

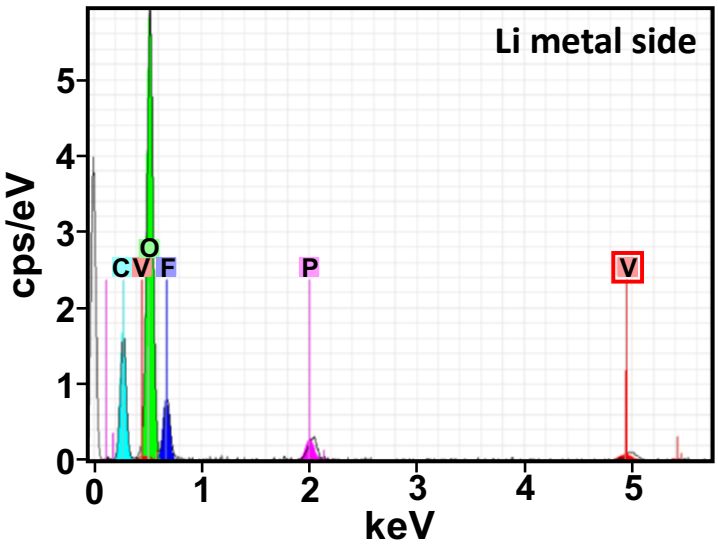

Figure S9. EDX showing that a deposited V on the Li-metal counter of $(NH_4)_2V_7O_{16}$/Li cell after 50 cycles (20 mA g^{-1} at 25 °C).

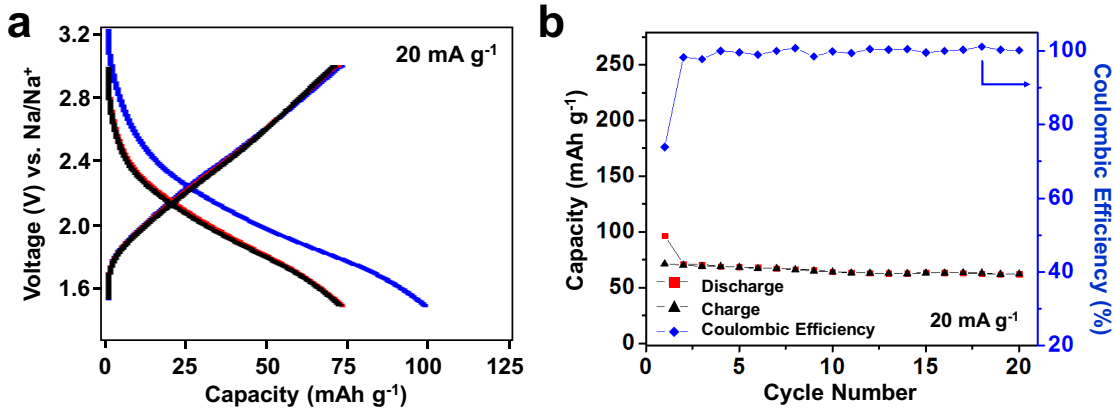

Figure S10. Electrochemical characterization of the $(NH_4)_2V_7O_{16}$//Na at 25 °C (cut-off voltage of 1.5−3.0 V vs Na/Na^+). (a) Initial three-cycles of galvanostatic discharge and charge profiles at a current density of 20 mA g^{-1}. (b) Cycle performance at a current density of 20 mA g^{-1} over 20 cycles.

Table S1. Data collection information and refinement parameters for $(NH_4)_2V_7O_{16}$ obtained from the single-crystal XRD data.

Formula	$(NH_4)_2V_7O_{16}$
Crystal color	Black
Formula weight	648.65
Crystal system	Triclinic,
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å)	a = 6.1480(6), b = 6.1434(5), c = 18.0309(17)
(°)	α = 95.621(3), β = 93.018(3), γ = 89.971(3)
Unit cell volume (Å^3)	676.80 Å^3
Z	2
Calculated density (g/cm^3)	3.183
Abs. Coef. μ (MoKα) (mm^{-1})	4.718 mm^{-1}
F(000)	622
Temperature (K)	298
Crystal size (mm^3)	0.03×0.03×0.002
Data collection	Bruker SAINT APEXII CCD Graphite monochromator
Radiation type, (Å)	Mo Kα, λ = 0.71076
Absorption correction	Multi-Scan (SADABS; Bruker), DIFABS
Rel. Tranm. Coeff. Range	0.76-1.00 (DIFABS)
Solution by	Direct method (SHELXS97)
Theta range for data collection	3.318° ≤ θ ≤ 32.297°
Index ranges	-8 ≤ h ≤ 7, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24
Reflections collected	16488
Independent reflection	3584
Observed reflection I > 3σ(I)	1694
R_{int} (%)	3.3 % (I > 10σ(I)), 17.3 % (10σ(I) > I > 3σ(I))
Restraints / Parameters	231 / 226
Refinement method	Full matrix least-squares on F^2
Goodness-of-fit on F^2	0.9770
Final R indices (I > 3σ(I))	R_p = 0.0612, R_{wp} = 0.1090
$(\Delta/\sigma)_{max}$	0.0001036
Largest residual peak and hole (e·Å^{-3})	1.36 and -2.34

Table S2. Selected interatomic distances (Å) of $(NH_4)_2V_7O_{16}$ obtained from single-crystal XRD data. The filled in green are a dangling bond between V–O in VO_5.

Atom pair	Distance(Å)	Atom pair	Distance(Å)
V(1)-O(13)	1.660(12)	V(1)-O(3)	2.026(9)
V(1)-O(1)	2.065(9)	V(1)-O(7)	1.939(9)
V(1)-O(8)	1.929(9)		
V(2)-O(1)	1.866(10)	V(2)-O(7)	1.754(9)
V(2)-O(9)	1.612(9)	V(2)-O(14)	1.969(10)
V(3)-O(5)	1.666(11)	V(3)-O(3)	1.883(9)
V(3)-O(8)	2.087(9)	V(3)-O(7)	2.057(9)
V(3)-O(12)	1.696(9)		
V(4)-O(4)	1.604(11)	V(4)-O(3)	1.935(9)
V(4)-O(12)	1.999(9)	V(4)-O(8)	1.974(9)
V(4)-O(1)	1.988(8)		
V(5)-O(16)	1.653(11)	V(5)-O(2)	2.033(9)
V(5)-O(6)	1.834(9)	V(5)-O(9)	1.976(9)
V(5)-O(10)	2.026(9)		
V(6)-O(15)	1.636(11)	V(6)-O(2)	1.967(9)
V(6)-O(6)	1.867(9)	V(6)-O(10)	1.846(8)
V(6)-O(14)	2.068(9)		
V(7)-O(11)	1.661(11)	V(7)-O(9)	1.969(9)
V(7)-O(10)	2.060(9)	V(7)-O(2)	1.873(9)
V(7)-O(14)	2.039(9)		
N(1)-H(3)	0.916	N(1)-H(4)	1.019
N(1)-H(7)	0.955	N(1)-H(8)	0.949
N(2)-H(1)	1.100	N(2)-H(2)	1.080
N(2)-H(5)	0.955	N(2)-H(6)	0.949

Table S3. Anisotropic displacement parameters of $(NH_4)_2V_7O_{16}$ obtained from single-crystal XRD data.

Atom	U_{11} (Å^{2}x10^2)	U_{22} (Å^{2}x10^2)	U_{33} (Å^{2}x10^2)	U_{23} (Å^{2}x10^2)	U_{13} (Å^{2}x10^2)	U_{12} (Å^{2}x10^2)
V1	0.42(11)	0.50(12)	0.48(11)	0.07(9)	-0.11(9)	0.11(9)
V2	0.58(11)	0.55(11)	0.50(11)	0.07(9)	-0.03(9)	0.12(9)
V3	0.35(11)	0.30 (12)	0.43(11)	-0.14(9)	-0.01(9)	0.11(9)
V4	0.47(11)	0.47(11)	0.55(12)	-0.02(9)	0.11(9)	0.00(9)
V5	0.52(10)	0.76(11)	0.55(9)	-0.03(9)	0.05(9)	-0.03(9)
V6	0.46(11)	0.53(12)	0.58(11)	0.09(9)	0.11(9)	-0.05(9)
V7	0.49(10)	0.68(10)	0.45(9)	0.01(9)	-0.02(9)	0.06(9)
O1	0.7(3)	0.4(4)	0.5(3)	0.0(3)	-0.1(3)	0.0(3)
O2	0.8(2)	0.6(3)	0.7(2)	-0.2(2)	0.0(3)	0.0(3)
O3	1.1(3)	0.8(3)	0.9(3)	0.3(3)	0.0(3)	-0.4(3)
O4	1.4(3)	1.6(4)	1.2(3)	-0.4(3)	-0.3(3)	0.0(3)
O5	1.3(3)	1.5(4)	1.1(3)	-0.3(3)	-0.1(3)	0.0(3)
O6	0.9(2)	0.7(3)	0.8(2)	0.1(3)	0.0(3)	0.2(3)
O7	0.9(3)	0.6(4)	0.9(3)	0.1(3)	0.0(3)	0.3(3)
O8	0.7(2)	0.5(3)	0.6(2)	0.0(3)	0.4(3)	-0.1(3)
O9	0.9(3)	0.7(4)	0.8(3)	0.0(3)	-0.4(3)	0.0(3)
O10	0.8(2)	0.5(3)	0.6(2)	-0.07(19)	-0.08(19)	-0.20(19)
O11	1.4(3)	1.8(4)	1.4(3)	-0.2(3)	-0.2(3)	-0.0(3)
O12	1.0(3)	0.8(3)	1.0(3)	-0.3(3)	0.0(3)	-0.1(3)
O13	1.5(3)	1.6(3)	1.5(3)	-0.4(3)	-0.4(3)	-0.2(3)
O14	1.1(3)	0.8(4)	1.0(3)	0.0(3)	-0.33(19)	-0.1(3)
O15	1.4(3)	1.3(4)	1.1(3)	-0.1(3)	-0.3(3)	0.0(3)
O16	1.3(3)	1.5(4)	1.2(3)	0.0(3)	-0.1(3)	-0.2(3)
N1	2.0(3)	2.4(4)	2.2(3)	-0.4(4)	-0.4(4)	0.3(3)
N2	1.8(3)	2.1(5)	1.8(4)	0.2(4)	0.4(4)	-0.3(4)