Electronic Supplementary Information for

A vanadium-based oxide-phosphate-pyrophosphate framework as a 4 V electrode material for K-ion batteries

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Table. S1 Refined structural parameters of pristine $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ obtained from Rietveld refinement of synchrotron XRD data.

R_{wp} = 4.48%

1st phase (KVPP): 97.2 mass%

Space group: *Pnma*

a = 6.97269(6) Å, *b* = 13.39710(10) Å, *c* = 14.23770(11) Å

R_B = 2.20%, R_F = 0.92%

Atom	site	*x*	*y*	*z*	*g*	B_{iso} / Å^2
K1	8d	0.1013(2)	0.00896(15)	0.33586(13)	0.980(2)	1.5
K2	4c	0.1215(3)	0.25	0.50876(18)	0.989(2)	1.5
V1	8d	0.15852(18)	0.12489(10)	0.07835(10)	1	0.5
V2	4c	0.2442(3)	0.25	0.75965(14)	1	0.5
P1	8d	0.0383(3)	0.59833(18)	0.11843(16)	1	1.0
P2	4c	0.360(1)	0.25	0.2407(5)	0.5	1.0
P3	4c	0.2796(9)	0.25	0.2617(5)	0.5	1.0
O1	8d	0.3359(6)	0.0646(3)	0.0320(3)	1	1.0
O2	4c	0.2224(8)	0.25	0.0421(4)	1	1.0
O3	8d	0.0290(6)	0.0115(3)	0.1449(2)	1	1.0
O4	8d	0.0506(6)	0.6161(3)	0.0111(3)	1	1.0
O5	8d	0.2745(6)	0.1544(3)	0.2066(2)	1	1.0
O6	4c	0.4596(9)	0.25	0.8023(4)	1	1.0
O7	8d	0.3527(7)	0.6445(3)	0.3392(3)	1	1.0
O8	8d	0.2190(6)	0.6443(3)	0.1622(3)	1	1.0
O9	4c	0.4061(9)	0.25	0.3462(4)	1	1.0
O10	4c	0.071(1)	0.25	0.3114(9)	0.5	1.0

Table. S2 V-O bond lengths in the refined structure of as-prepared $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$.

Polyhedron	Bond	Bond length / Å
Square pyramid $V1O_5$ (octahedron)	V1-O1	1.618(5)
	V1-O2	1.809(3)
	V1-O3	2.004(5)
	V1-O4	1.940(5)
	V1-O5	2.057(5)
	V1-O9	2.658(6)
Octahedron $V2O_6$	V2-O6	1.622(8)
	V2-O6	2.168(8)
	V2-O7	1.933(5)
	V2-O7	1.933(5)
	V2-O8	1.999(5)
	V2-O8	1.999(5)

Table. S3 Refined structural parameters of $K_x(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ at the charged state, which were obtained from Rietveld refinement of synchrotron XRD data of the KVPP electrode charged to 4.5 V.

R_{wp} = 6.94%

Space group: *Pnma*

a = 7.1372(2) Å, b = 13.0433(4) Å, c = 14.1399(4) Å, V = 1316.34(7) Å^3

R_B = 7.58%, R_F = 3.49%

Atom	site	*x*	*y*	*z*	*g*	B_{iso} / Å^2
K1	8d	0.1158(8)	0.0308(4)	0.3424(3)	0.646(2)	1.6
K2	4c	0.1325(12)	0.25	0.5060(6)	0.507(8)	1.6
V1	8d	0.1604(4)	0.1233(2)	0.0791(2)	1	0.5
V2	4c	0.2468(6)	0.25	0.7584(3)	1	0.5
P1	8d	0.0299(8)	0.5985(3)	0.1221(3)	1	1.0
P2	4c	0.376(2)	0.25	0.2465(13)	0.5	1.0
P3	4c	0.271(2)	0.25	0.2680(12)	0.5	1.0
O1	8d	0.3226(13)	0.0576(6)	0.0358(6)	1	1.0
O2	4c	0.2350(16)	0.25	0.0333(10)	1	1.0
O3	8d	0.0370(13)	0.0177(7)	0.1468(6)	1	1.0
O4	8d	0.0199(14)	0.6158(6)	0.0143(6)	1	1.0
O5	8d	0.2874(14)	0.1572(7)	0.2043(6)	1	1.0
O6	4c	0.496(2)	0.25	0.8005(8)	1	1.0
O7	8d	0.3520(15)	0.6423(7)	0.3381(6)	1	1.0
O8	8d	0.2077(14)	0.6484(7)	0.1628(6)	1	1.0
O9	4c	0.4258(18)	0.25	0.3531(10)	1	1.0
O10	4c	0.046(4)	0.25	0.313(2)	0.5	1.0

Table. S4 Refined structural parameters of $K_x(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ at the discharged state, which were obtained from Rietveld refinement of synchrotron XRD data of the KVPP electrode discharged to 2.0 V.

R_{wp} = 7.86%

Space group: *Pnma*

a = 6.98358(12) Å, *b* = 13.3883(2) Å, *c* = 14.2489(2) Å, *V* = 1332.25(3) Å^3

R_B = 7.90%, R_F = 4.84%

Atom	site	*x*	*y*	*z*	*g*	B_{iso} / Å^2
K1	8d	0.1031(4)	0.0083(2)	0.3366(2)	0.981(3)	1.5
K2	4c	0.1260(5)	0.25	0.5092(2)	1.007(4)	1.5
V1	8d	0.1597(3)	0.12422(18)	0.07882(17)	1	0.5
V2	4c	0.2469(5)	0.25	0.7592(2)	1	0.5
P1	8d	0.0344(5)	0.5983(3)	0.1182(2)	1	1.0
P2	4c	0.3589(18)	0.25	0.2425(10)	0.5	1.0
P3	4c	0.2782(16)	0.25	0.2614(10)	0.5	1.0
O1	8d	0.3345(10)	0.0649(5)	0.0321(5)	1	1.0
O2	4c	0.2258(13)	0.25	0.0429(7)	1	1.0
O3	8d	0.0302(11)	0.0155(5)	0.1478(5)	1	1.0
O4	8d	0.0452(10)	0.6146(5)	0.0111(5)	1	1.0
O5	8d	0.2801(11)	0.1519(5)	0.2060(5)	1	1.0
O6	4c	0.4590(17)	0.25	0.7989(7)	1	1.0
O7	8d	0.3564(12)	0.6463(5)	0.3404(5)	1	1.0
O8	8d	0.2171(11)	0.6454(5)	0.1614(5)	1	1.0
O9	4c	0.4118(16)	0.25	0.3466(7)	1	1.0
O10	4c	0.061(3)	0.25	0.3136(15)	0.5	1.0

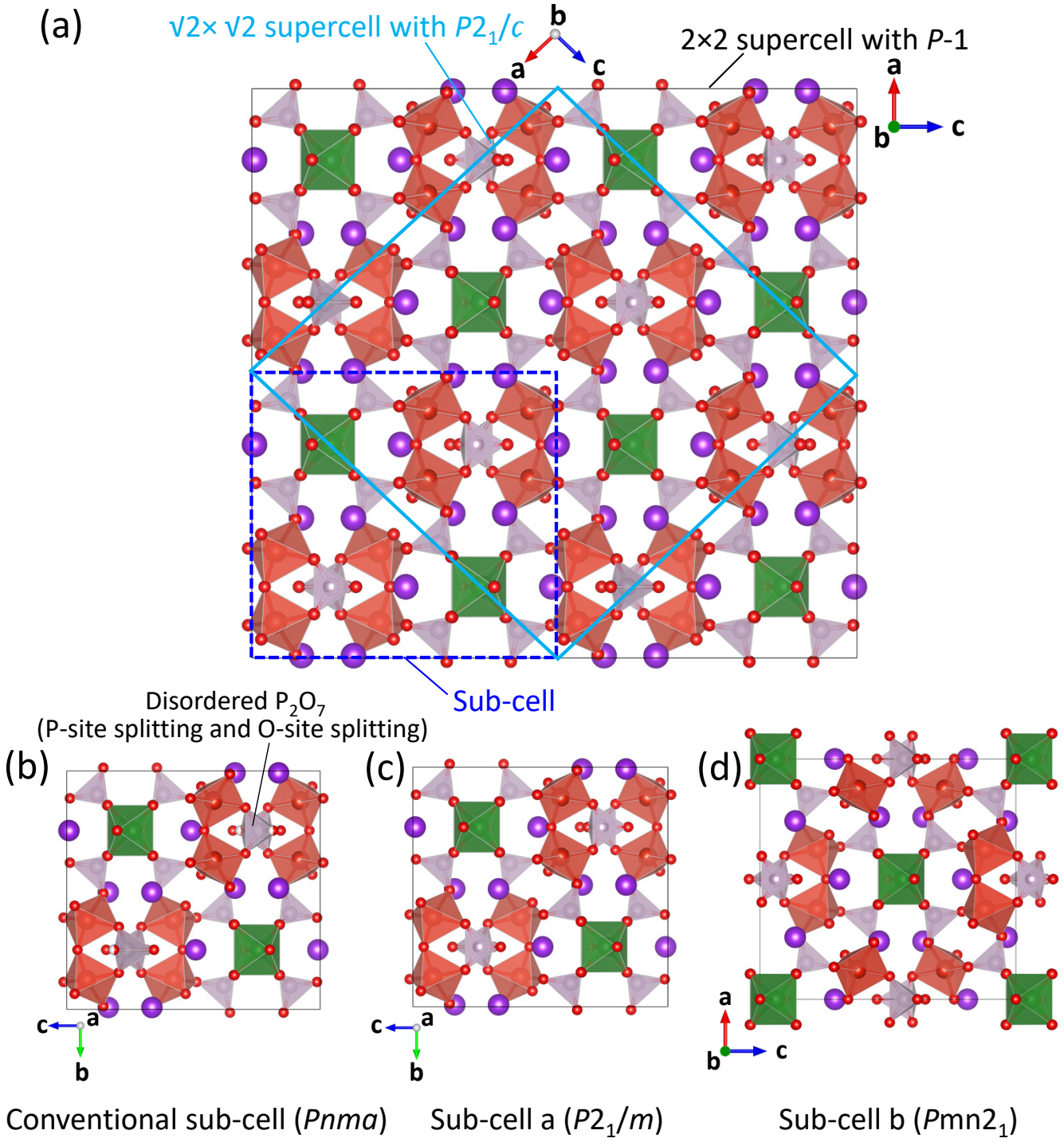

Fig. S1 Schematic illustrations of crystal structures for $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$. (a) Relationship between the conventional sub-cell and triclinic and monoclinic supercells. (b-d) Projected crystal structures of (b) conventional sub-cell (*Pnma*) having split P and O sites as disorderly located P_2O_7 units, monoclinic sub-cell a ($P2_1/m$), and orthorhombic sub-cell b ($Pmn2_1$). In the latter sub-cells and supercells, the P_2O_7 units are in order with no P-site splitting and no O-site splitting.

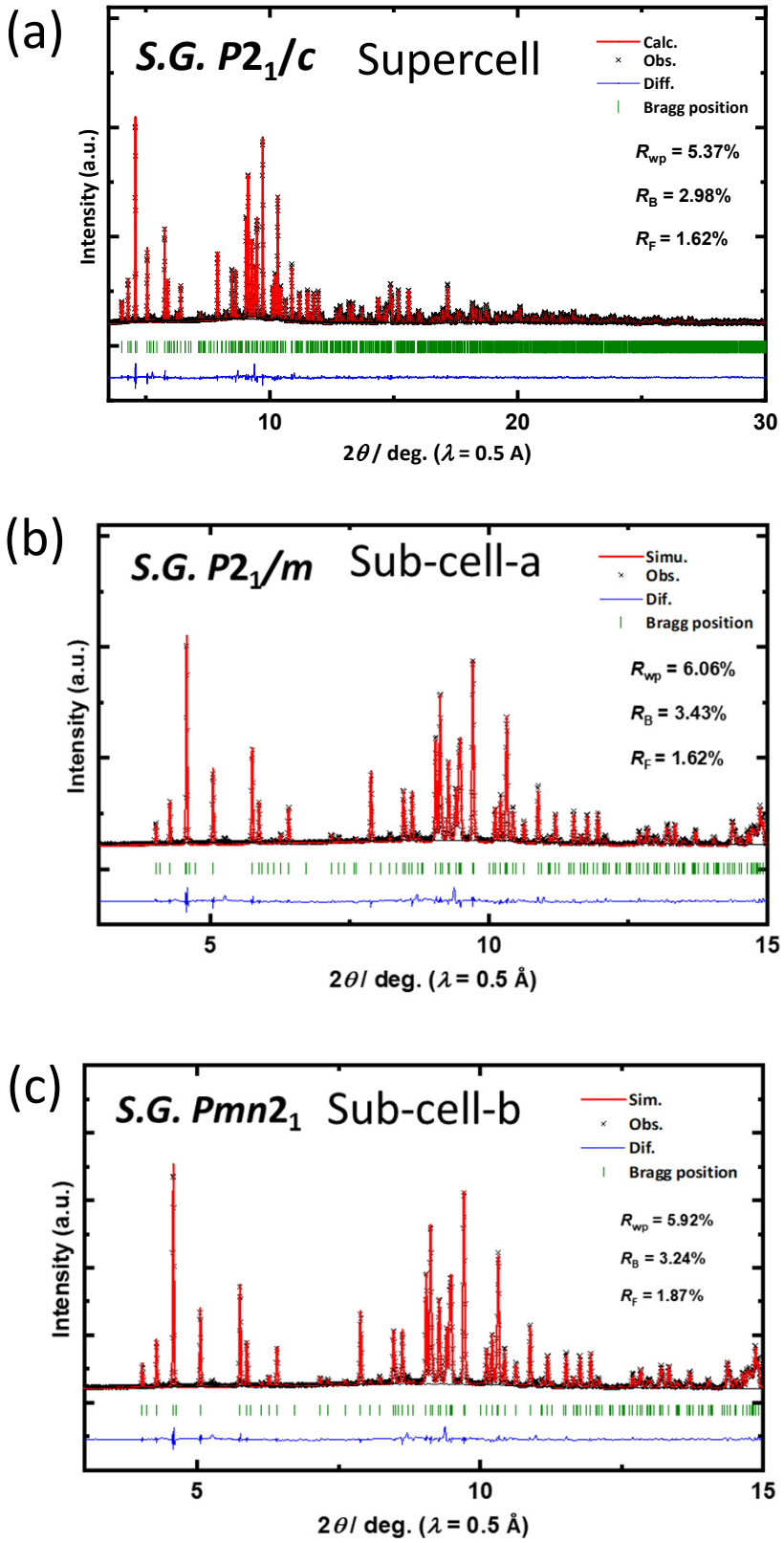

Fig. S2 Comparison of Rietveld refinement results for fitting the synchrotron XRD pattern of as-prepared $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ using different structural models: (a) monoclinic supercell ($P2_1/c$), (b) monoclinic sub-cell a ($P2_1/m$), and (c) orthorhombic sub-cell b ($Pmn2_1$). The structural models are illustrated in **Fig. S1**.

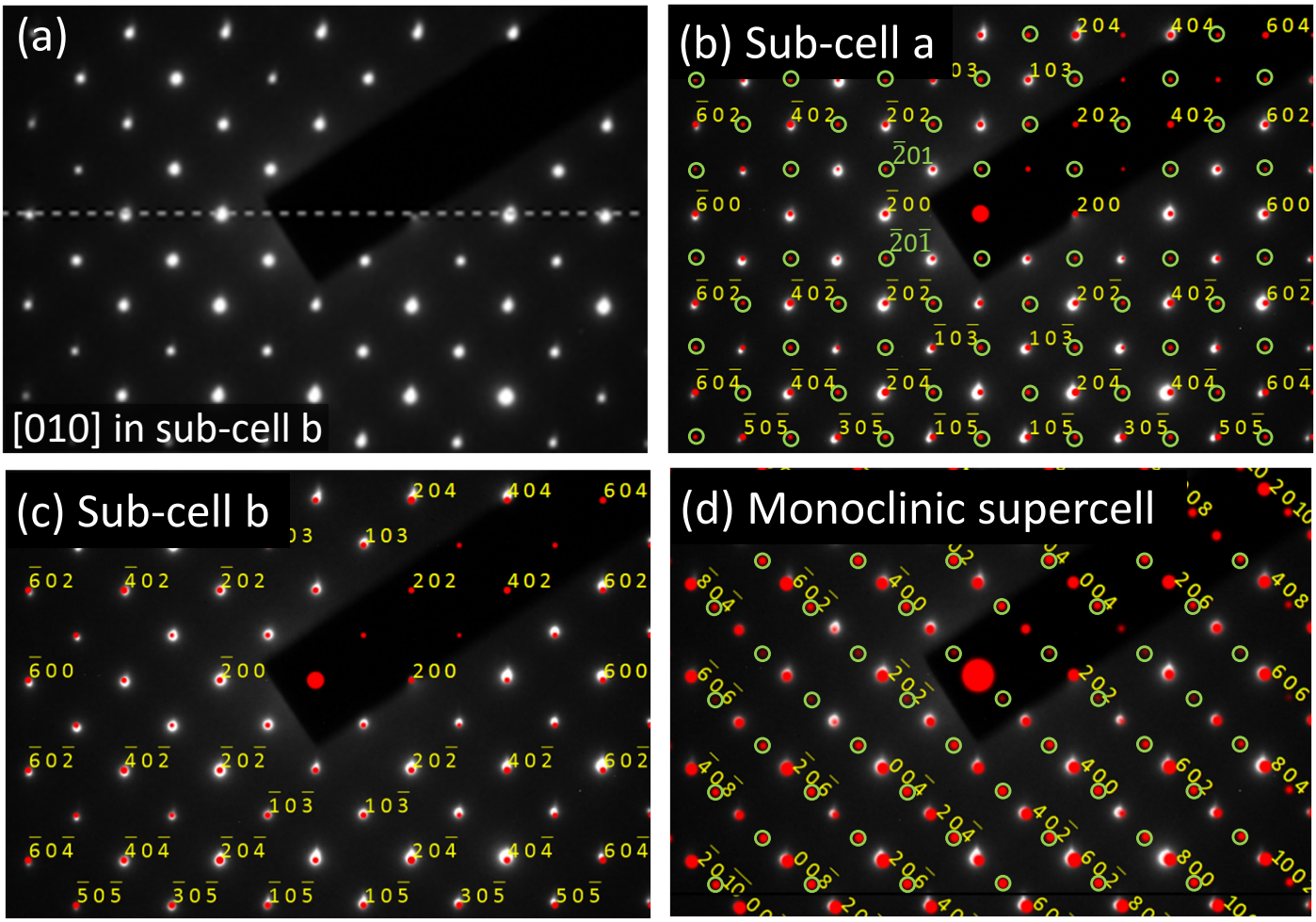

Fig. S3 Comparison of SAED patterns for $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$: (a) observed pattern and (b-d) simulated ones with (b) sub-cell a ($P2_1/m$), (c) sub-cell b ($Pmn2_1$), and (d) monoclinic supercell ($P2_1/c$). The structural models are shown in **Fig. S1**. For ease of understanding, the *a*- and *b*-axes of sub-cell a (the same as the conventional sub-cell) were transformed to be opposite and the same as sub-cell b. Green circles represent unobserved but simulated diffraction spots. The observed SAED pattern is the same as in **Fig. 2f**, where the crystal zone axis is labeled as [100] to match the conventional sub-cell.

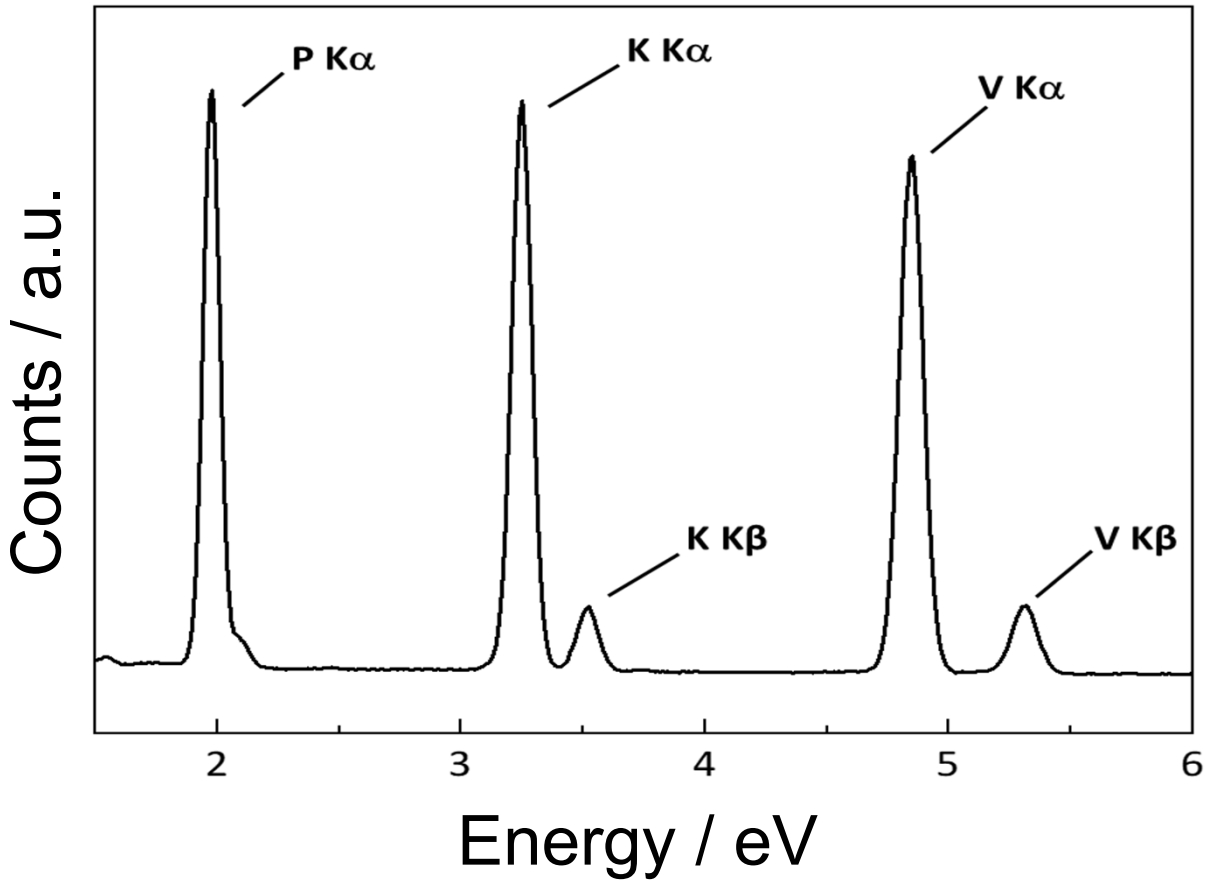

Fig. S4 TEM-EDX spectrum of as-prepared $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$.

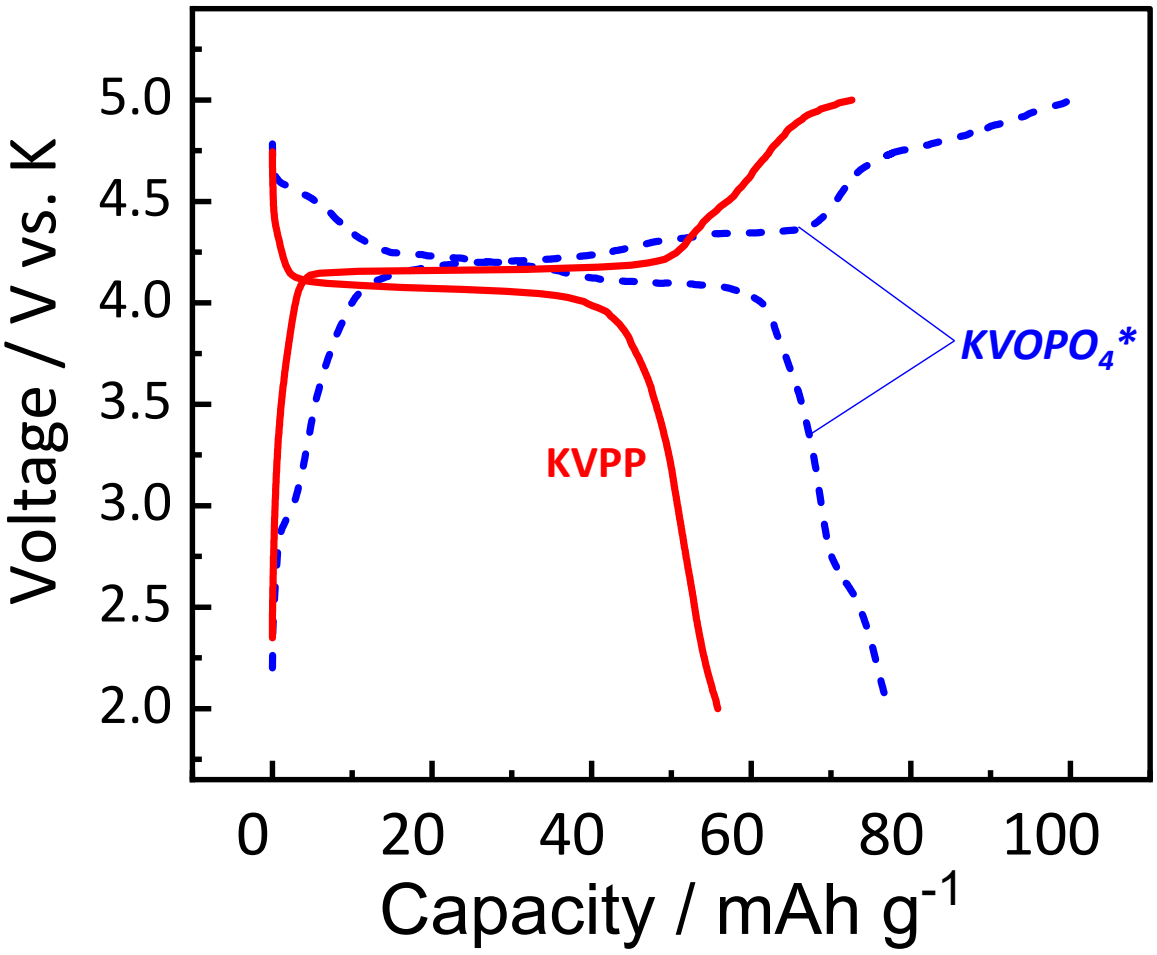

Fig. S5 Comparison of charge-discharge curves of $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ and $KVOPO_4$ electrodes at the 2nd cycle.

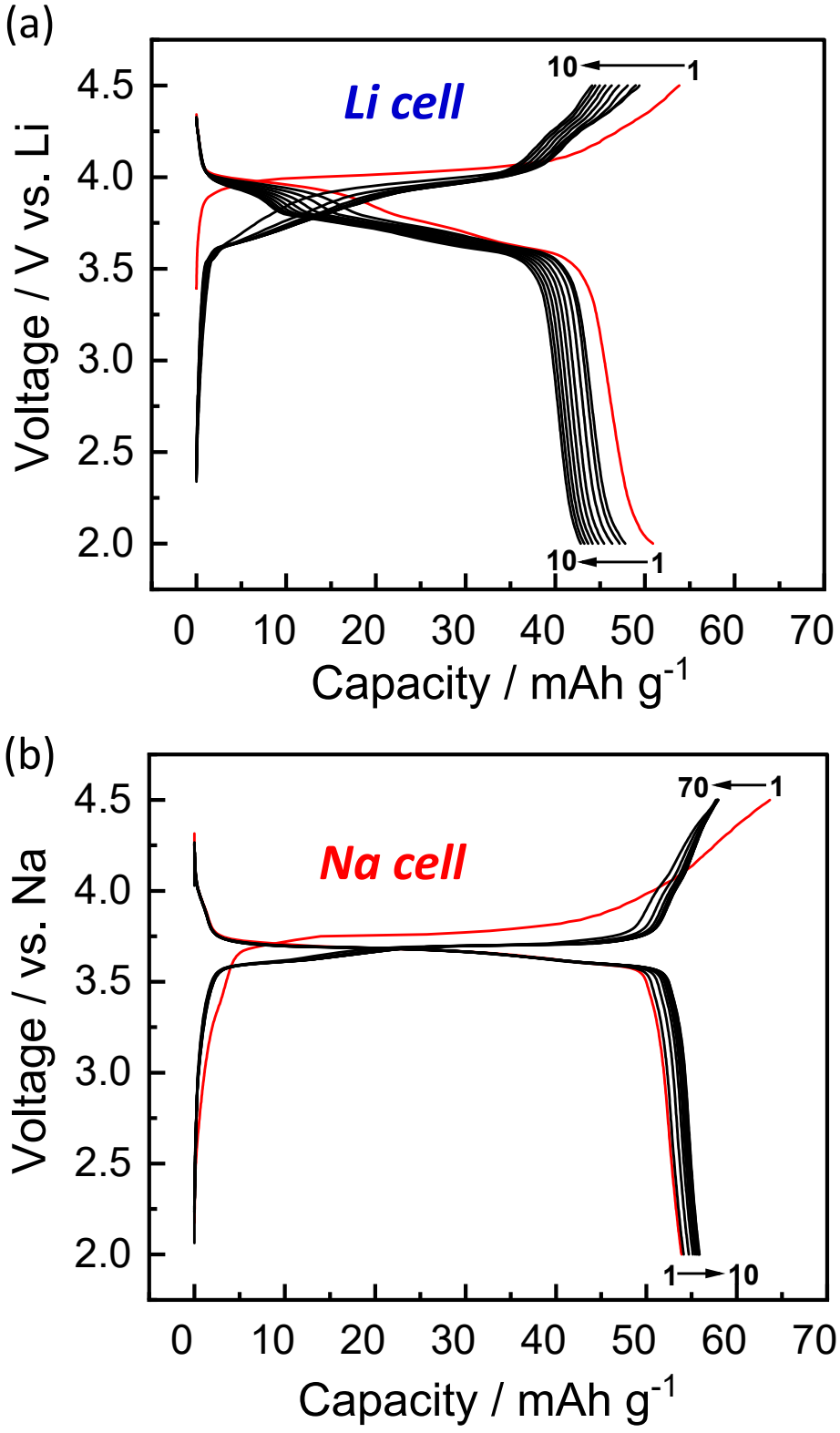

Fig. S6 Charge-discharge curves of $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ electrodes in (a) Li and (b) Na half-cells tested for first 10 cycles.

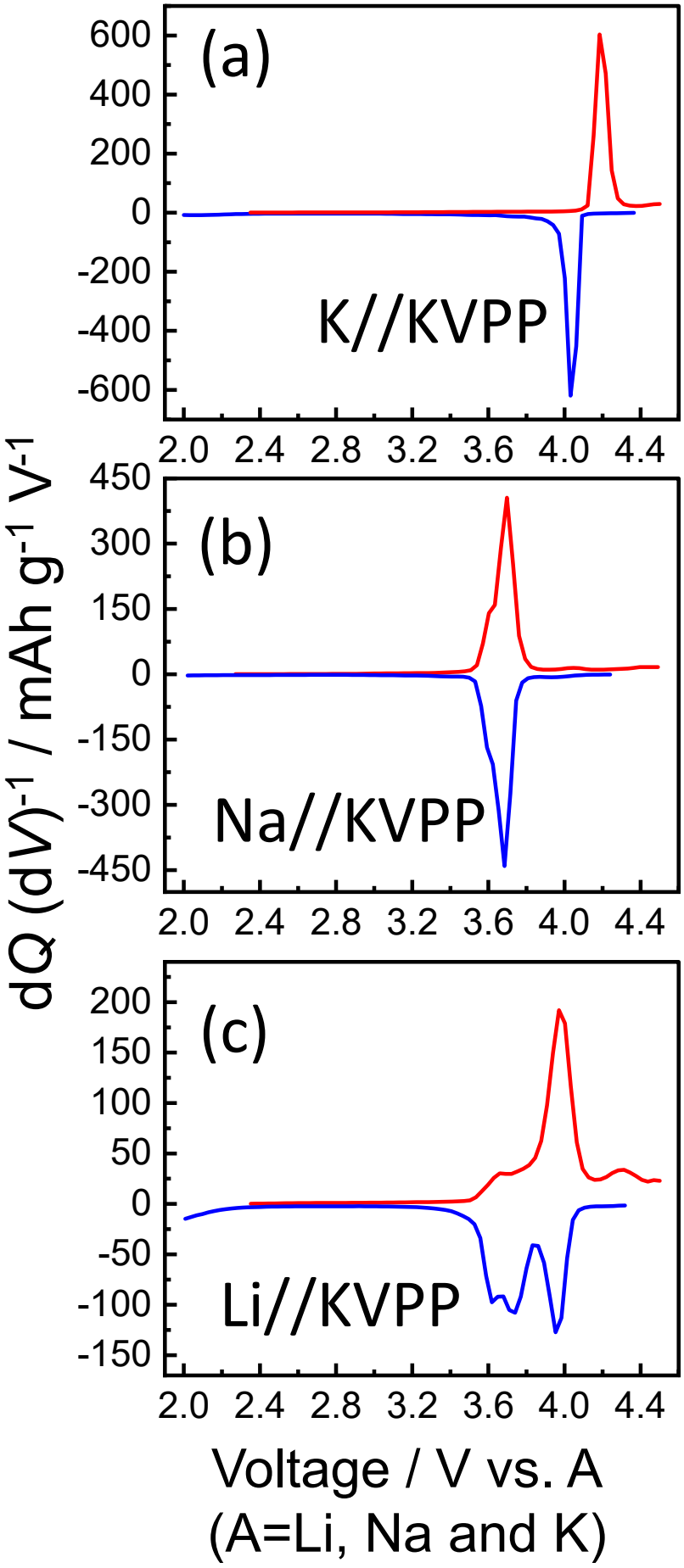

Fig. S7 Comparison of differential capacity vs. voltage plots of $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$ electrodes in Li, Na, and K half-cells at the 2nd cycle.

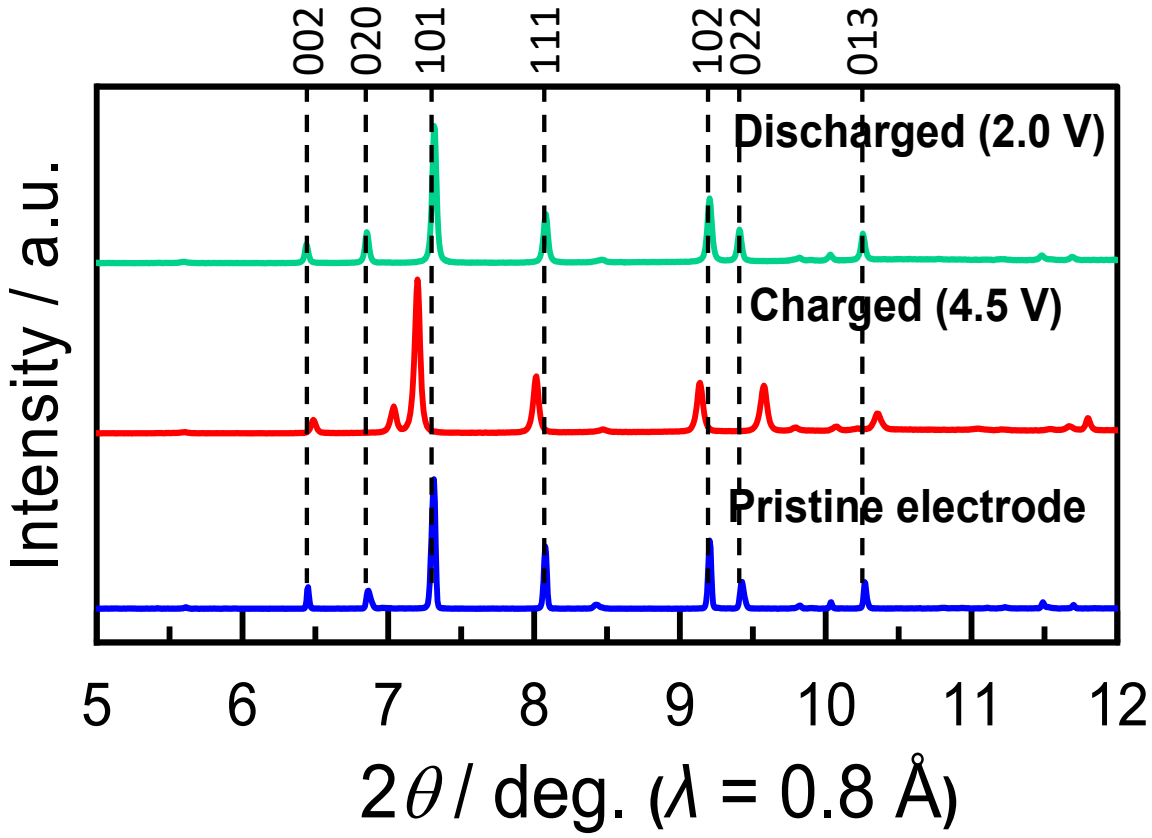

Fig. S8 Comparison of XRD patterns of charged and discharged electrodes with the pristine electrode of $K_x(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$.