Supporting Information

$KVPO_4F$ and $KVOPO_4$ toward 4 Volt-Class Potassium-Ion Batteries

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Table S1 Results of elemental analysis and Rietveld refinement.

(a) Elemental analyses of $KVPO_4F$ and $KVOPO_4$

	K	V	C
KVPF	0.99	1	0.14 wt%
KVPO	0.82	1	0.38 wt%

Quantitative analyses were performed by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPE-9800 (Shimazu Co.)) for K and V and Elemental Analysis (2400 CHNS/O Series II: PerkinElmer) for carbon.

(b) Results of Rietveld refinement of the obtained $KVPO_4F$

Space group $Pna2_1$		S = 1.02%	R_{wp} = 5.34%	R_B = 3.62%	R_F = 1.54%	
a = 12.80753(19) Å		b =6.38960(10) Å	c = 10.56621(13) Å		V = 864.68(2) Å^3	
atom	Wyckoff site	x	y	z	g	B
V1	4a	0.3816(2)	0.4959(8)	0	1	0.5
V2	4a	0.2489(4)	0.2582(7)	0.2459(10)	1	0.5
P1	4a	0.4982(7)	0.3283(6)	0.2575(13)	1	1.0
P2	4a	0.1835(4)	0.5047(13)	0.5015(11)	1	1.0
K1	4a	0.3802(5)	0.7830(7)	0.3070(7)	1	1.5
K2	4a	0.1041(4)	0.6966(6)	0.0671(7)	1	1.5
O1	4a	0.4821(12)	0.487(2)	0.1509(13)	1	1.0
O2	4a	0.5134(13)	0.483(2)	0.3869(13)	1	1.0
O3	4a	0.3962(12)	0.194(2)	0.2857(17)	1	1.0
O4	4a	0.5924(11)	0.203(2)	0.2430(16)	1	1.0
O5	4a	0.1058(14)	0.309(2)	0.5312(18)	1	1.0
O6	4a	0.1126(13)	0.689(3)	0.4715(15)	1	1.0
O7	4a	0.2601(11)	0.540(3)	0.6288(15)	1	1.0
O8	4a	0.2413(11)	0.469(3)	0.3911(16)	1	1.0
F1	4a	0.2767(11)	0.478(3)	0.1271(13)	1	1.0
F2	4a	0.2234(11)	0.034(3)	0.3757(11)	1	1.0

(c) Result of Rietveld refinement of the obtained $KVOPO_4$

Space group $Pna2_1$		S = 1.78	R_{wp} = 9.35%	R_B = 8.79%	R_F = 4.30%	
a = 12.7548(2) Å		b = 6.36557(11) Å	c = 10.5042(2) Å		V = 852.86(3) Å^3	
atom	Wyckoff site	x	y	z	g	B
V1	4a	0.3767(3)	0.5036(12)	0	1	0.5
V2	4a	0.2482(6)	0.2699(9)	0.2682(12)	1	0.5
P1	4a	0.5027(11)	0.3311(11)	0.2581(14)	1	1.0
P2	4a	0.1833(7)	0.500(2)	0.5269(11)	1	1.0
K1	4a	0.3842(9)	0.7837(15)	0.3271(12)	0.841(17)	1.5
K2	4a	0.1057(9)	0.7115(15)	0.0774(13)	= 1.64 - g(K1)	1.5
O1	4a	0.4932(19)	0.468(4)	0.151(2)	1	1.0
O2	4a	0.5279(14)	0.486(5)	0.3668(18)	1	1.0
O3	4a	0.3973(18)	0.201(3)	0.300(13)	1	1.0
O4	4a	0.5955(18)	0.190(3)	0.257(3)	1	1.0
O5	4a	0.1091(19)	0.323(3)	0.593(2)	1	1.0
O6	4a	0.106(2)	0.681(4)	0.495(3)	1	1.0
O7	4a	0.2425(16)	0.549(5)	0.656(2)	1	1.0
O8	4a	0.2674(15)	0.464(5)	0.416(2)	1	1.0
O9	4a	0.2523(16)	0.448(4)	0.172(2)	1	1.0
O10	4a	0.2093(15)	0.016(4)	0.394(2)	1	1.0

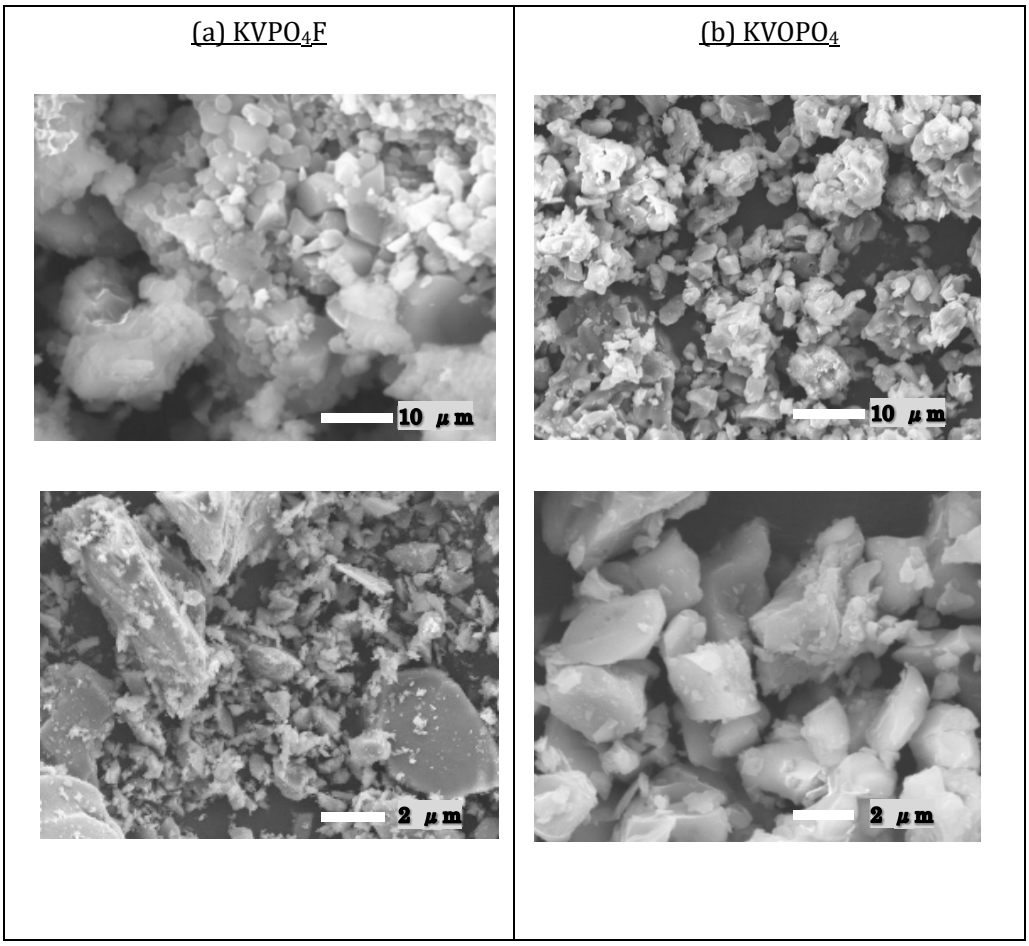
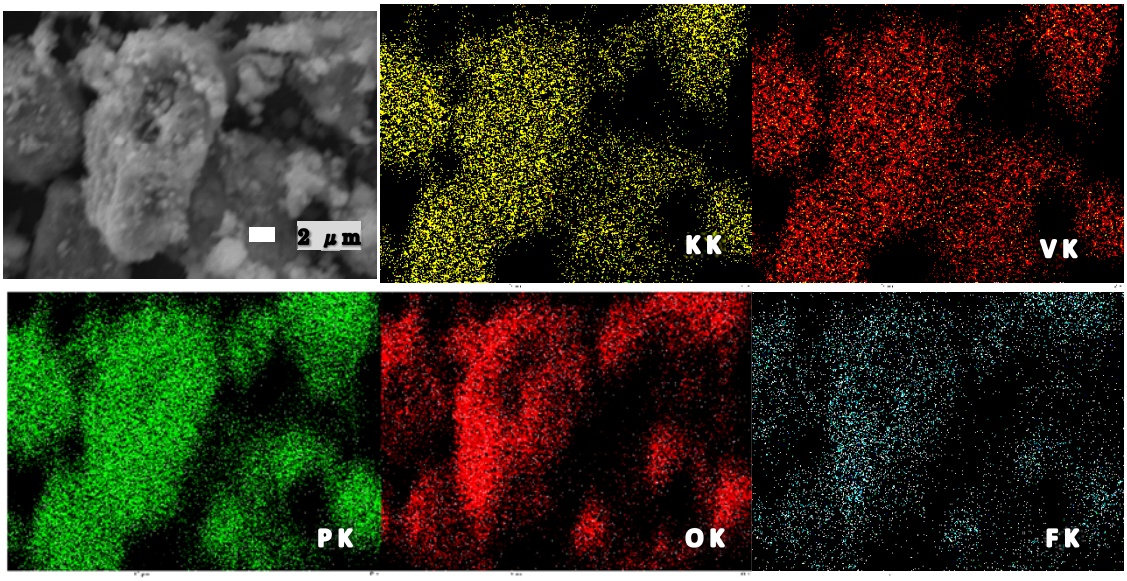


Figure S1 SEM images of (a) $KVPOF_4$ and (b)$KVOPO_4$.



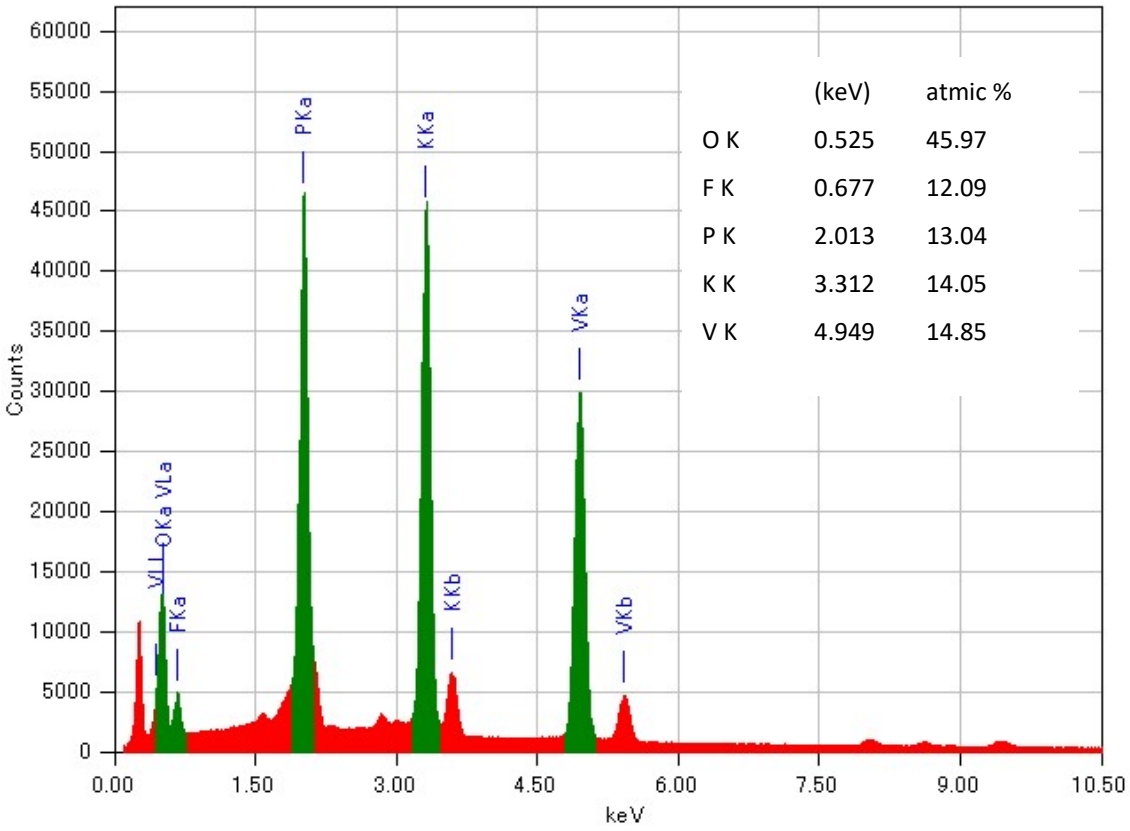
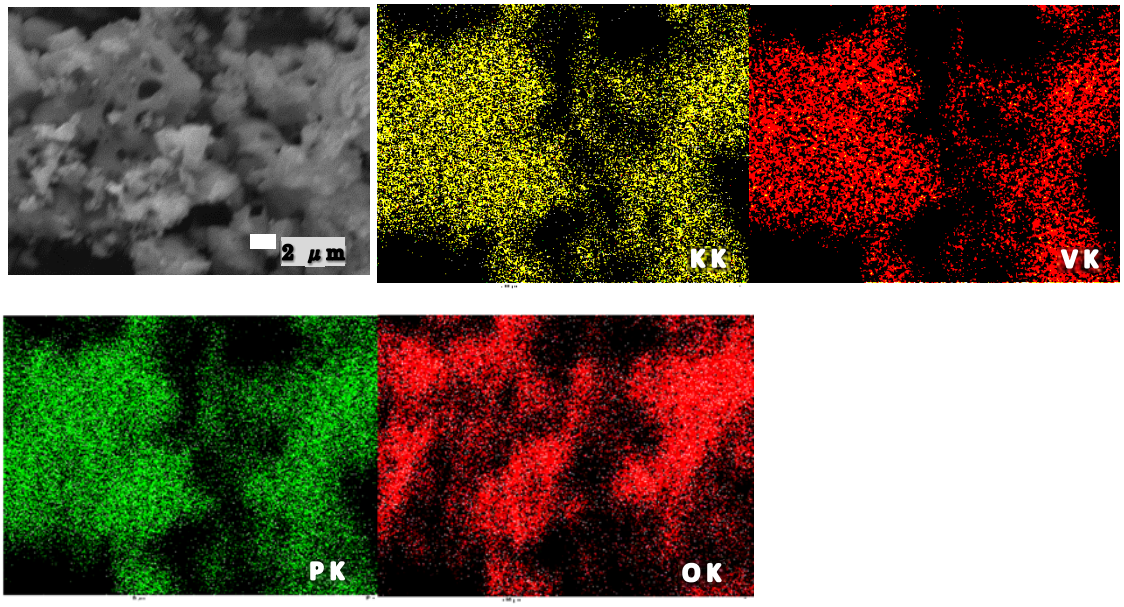


Figure S2 EDS mapping and spectrum measured by SEM for $KVPO_4F$.



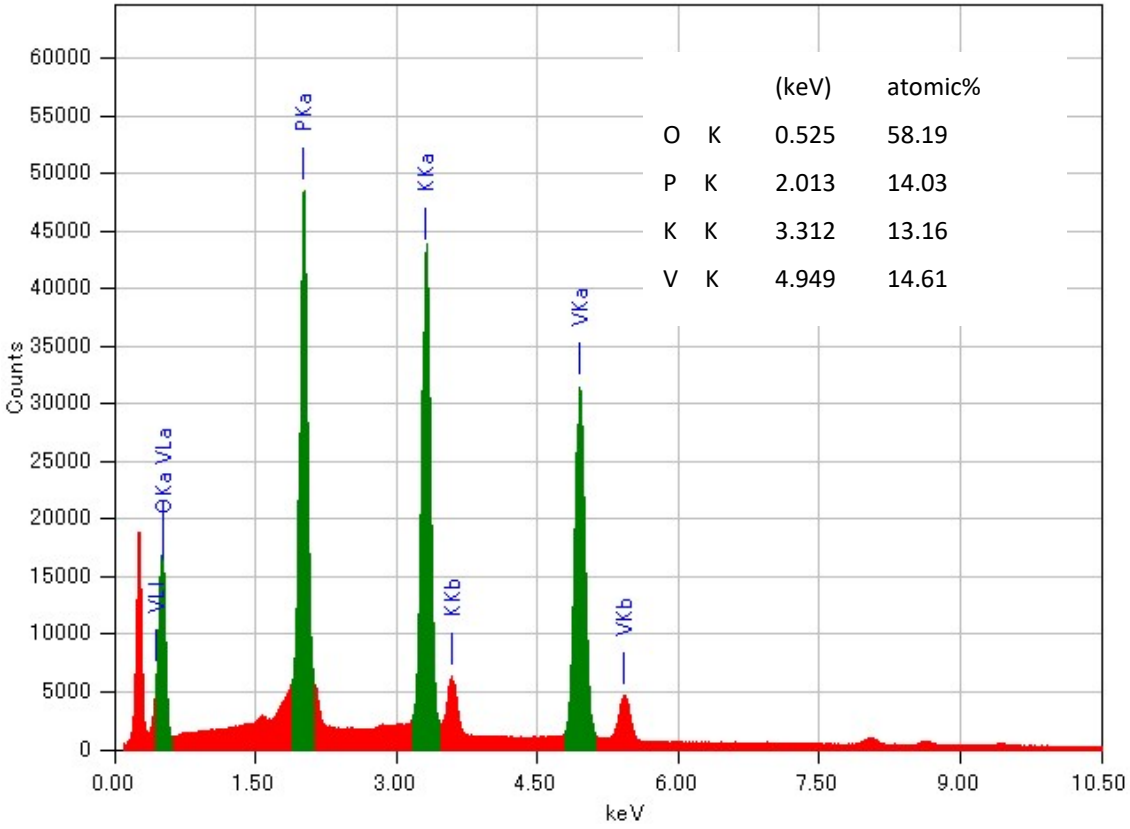


Figure S3 EDS mapping and spectrum measured by SEM for $KVOPO_4$.

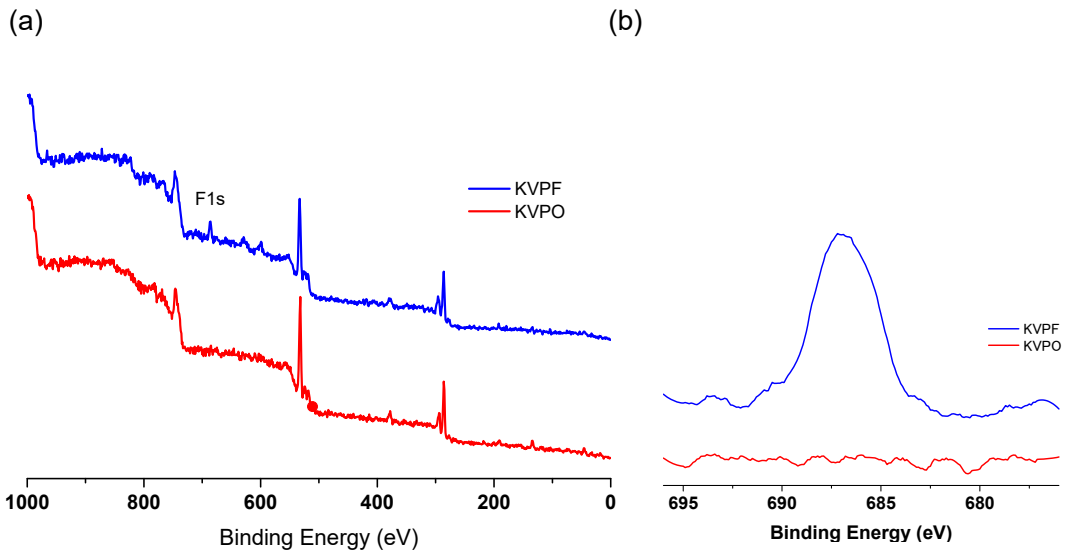


Figure S4 X-ray photoelectron spectroscopy spectra of (a) KVPF and KVPO in wide scan mode, and (b) F1s spectrum for KVPF (blue) and KVPO (red). The XPS spectra were obtained with Mg Kα without etching. A peak of F1s spectrum is only confirmed in KVPF, which is also clearly seen in the wide scan mode (Fig. S2(a))

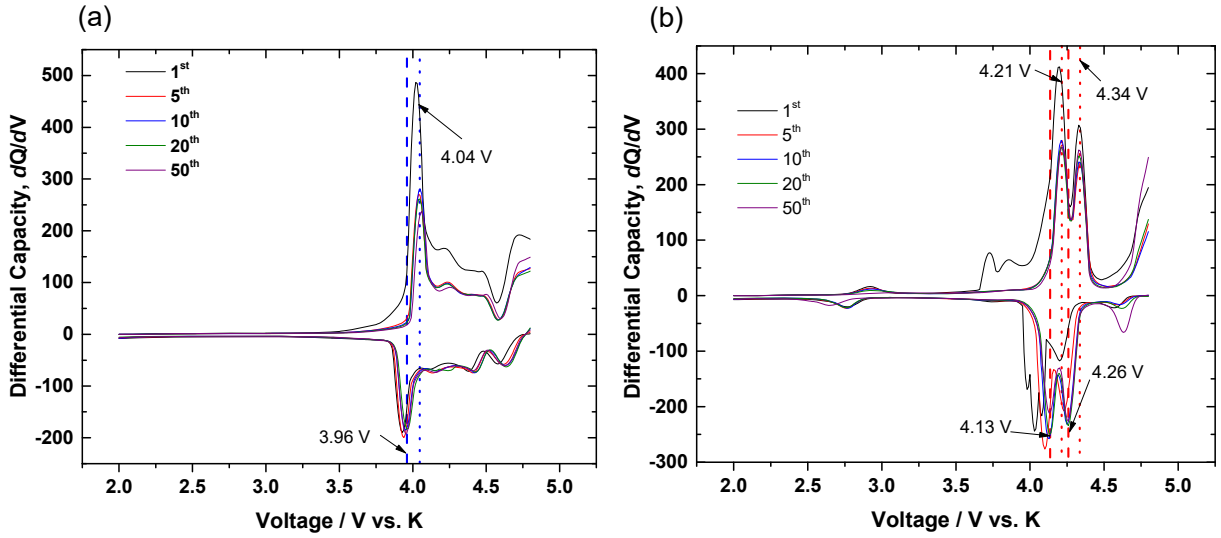


Figure S5 dQ/dV curves of (a)KVPF and (b)KVPO in the voltage range of 4.8 – 2.0 V. Large irreversible capacity at 1st cycle was observed in the both cases. The 1st dQ/dV curve was different from 2nd cycle in KVPO. Since the structural evolutions of KVPO are same between 1st and 2nd cycles in in-situ XRD, this difference would not be related to that of KVPO.

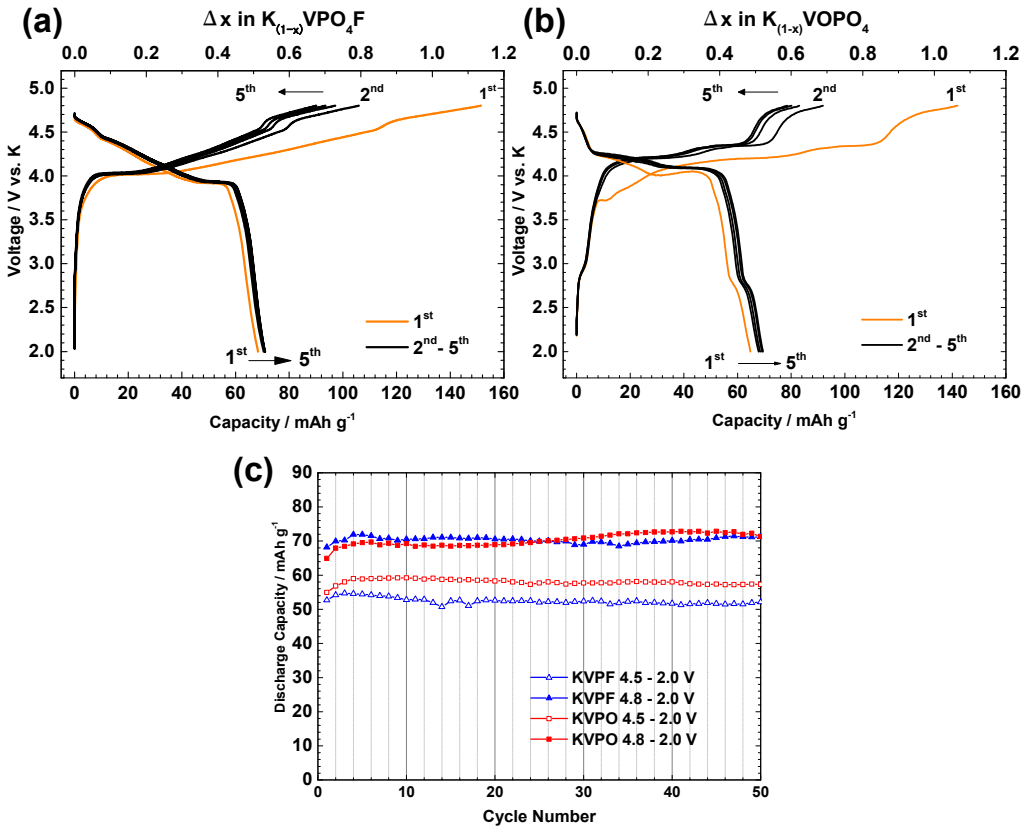


Figure S6 Charge and discharge profiles of (a) KVPF and (b) KVPO in 4.8 – 2.0, and (c) their cycle performance in 4.8 – 2.0 V and 4.5 – 2.0 V. Large irreversible capacity is observed at 1st cycle both in KVPF and KVPO, and the discharge capacity gradually increases and becomes stable after 5th cycle regardless of cut off voltage.

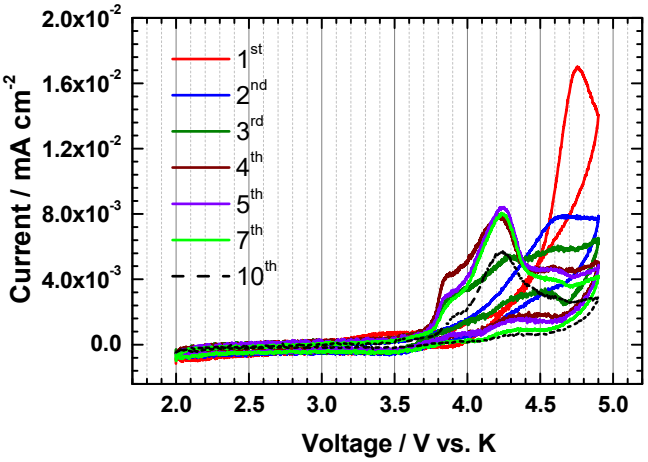


Figure S7 CV curves of 0.7 M KPF_6 in EC:DEC (1:1 v/v). A coin cell was assembled with Al foil as a working electrode against a metallic potassium counter electrode. Cyclic voltammetry measurement was carried out at a scanning spped of 0.5 mV s^{-1} in 2.0 – 4.9 V. Anodic peaks above 3.7 V appear in all cycles without corresponding cathodic peaks, suggesting continues electrolyte decomposition.

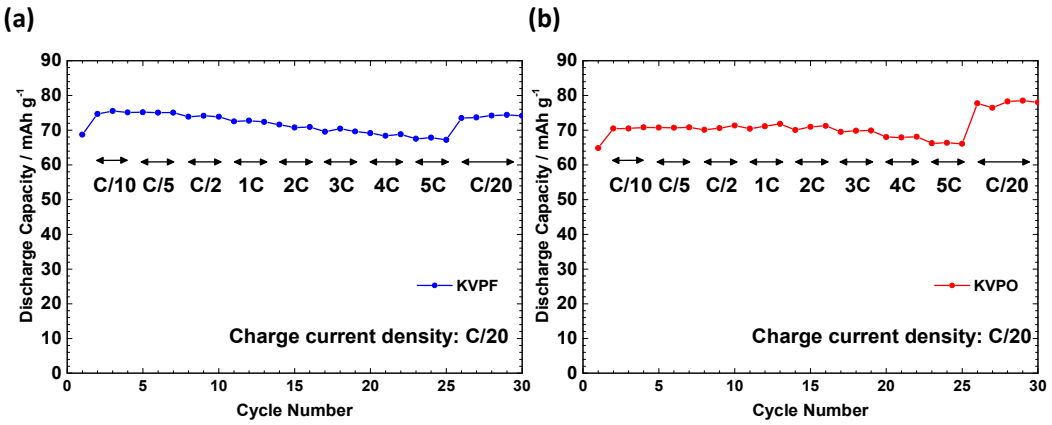


Figure S8 Discharge capacities of (a) KVPF and (b) KVPO under the increasing current from C/10 to 5C in the voltage range of 4.8 – 2.0 V. The 1st charge and discharge was cycled with C/20 (1C = 133.33 mA/g), and then the discharge current was changed from C/10 to 5C with fixed charge rate of C/20.

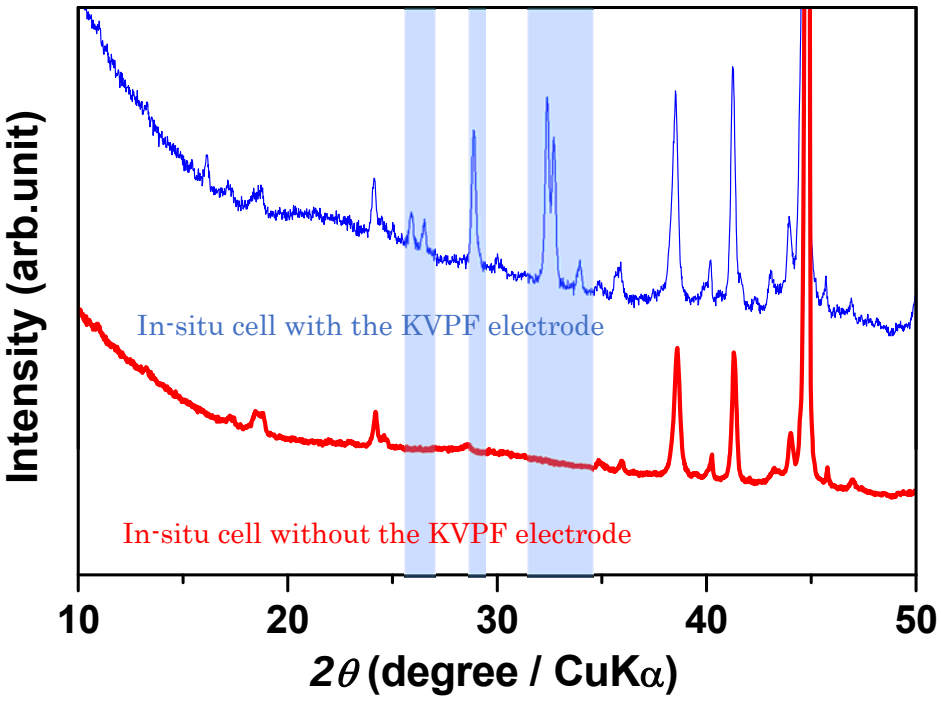


Figure S9 XRD patterns of the *in-situ* cell with (blue) and without (red) the KVPF electrode. The areas highlighted with blue indicate the main regions focused in the manuscript for structure change during potassiation in Fig. 3.

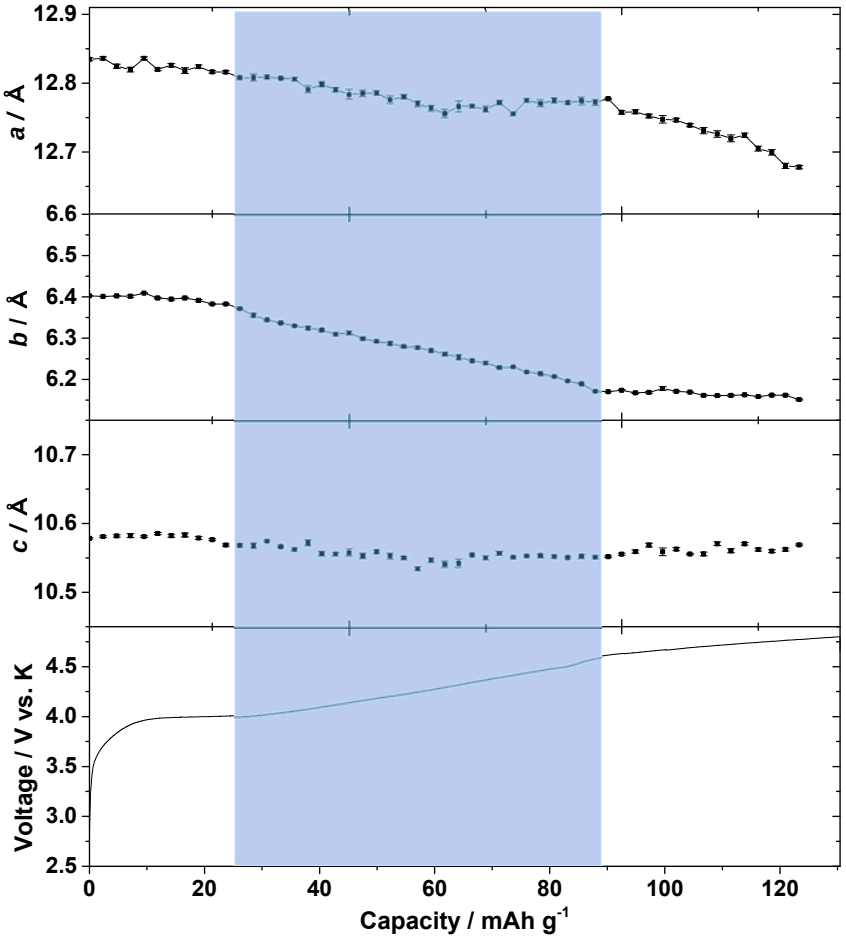


Figure S10 Lattice parameter changes for KVPF during the first potassium extraction. The parameters were calculated by means of CELLREF software. As seen in the regions separated with blue in the graph, the parameter change in the *a*, *b*, and *c* axis well corresponds to the charge profile of KVPF.

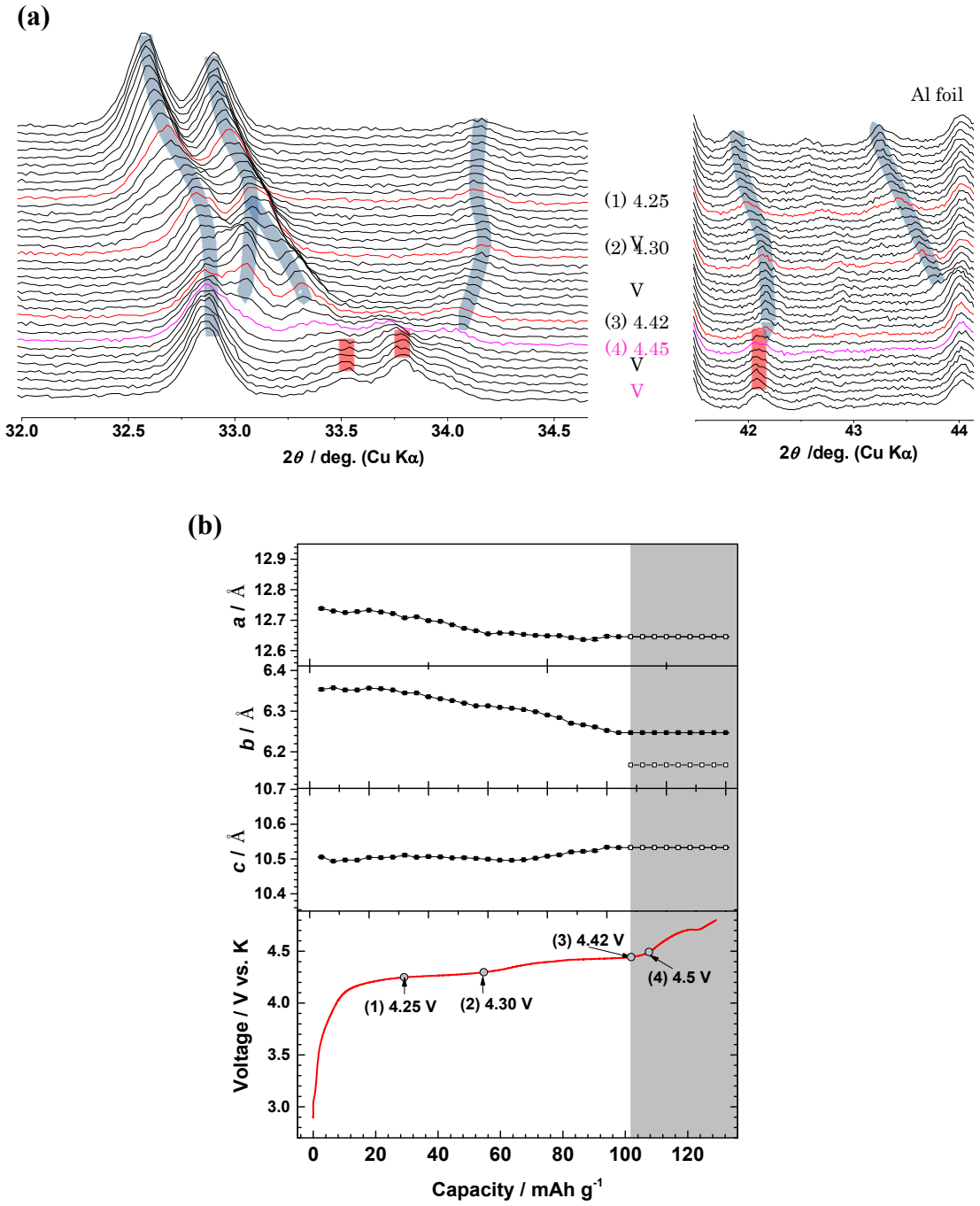


Figure S11 (a) Enlarged *operando* XRD patterns of KVPO during potassium extraction at 1st charge, and (b) the corresponding cell parameter change and charge profile. The parameters in the two phase region (gray color) are estimated values based on *operand* XRD data. The electrolyte decomposition might occur at the upper region after the step at 4.5 V due to less airtightness of the *in-situ* cell, leading a steep voltage increase around 4.7 V.

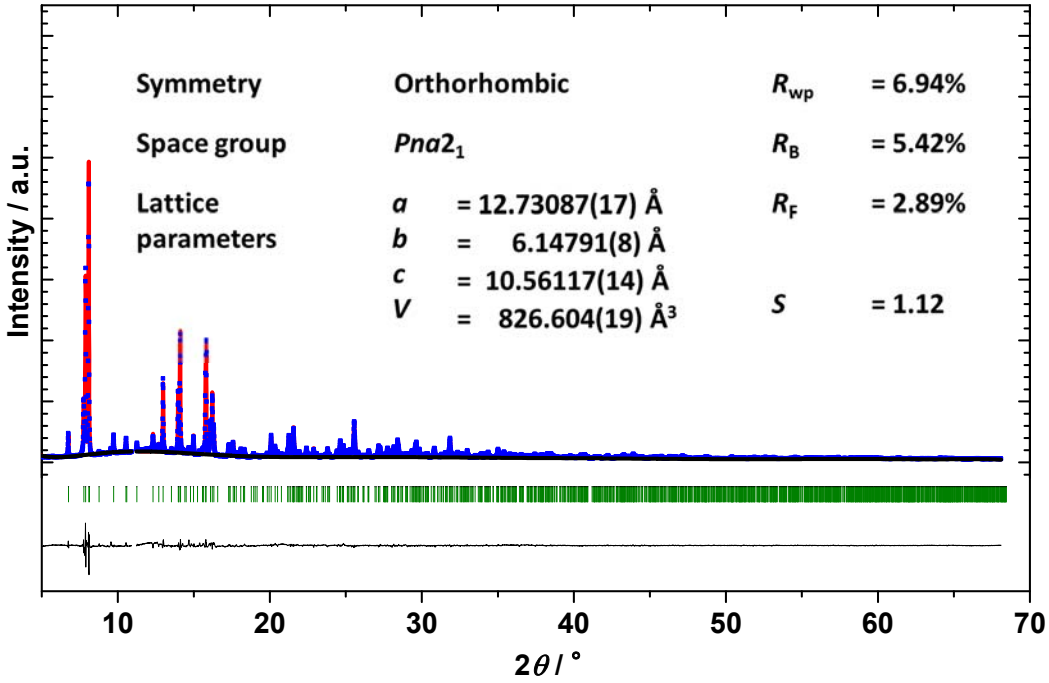


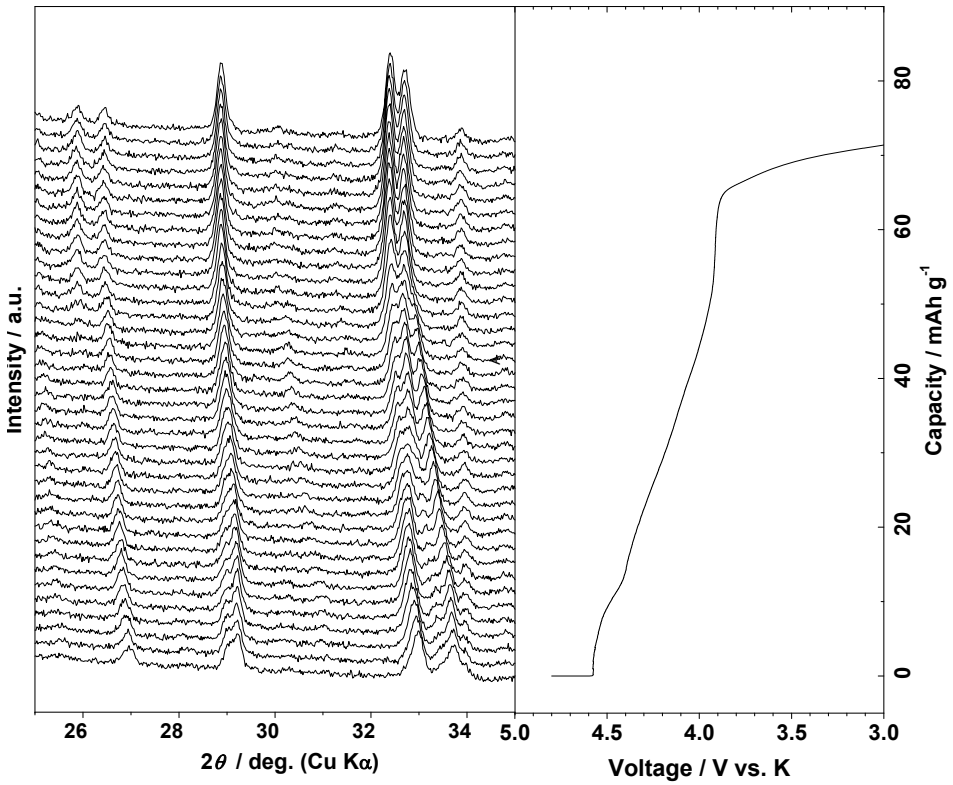
Figure S12 Result of Rietveld refinement for the KVPO electrode charged to 4.8 V. The blue dots and red lines represent experimental and calculated values, respectively. The black lines are the difference between the calculated and observed patterns and the vertical green bars correspond to the expected positions of Bragg reflections.

Table S2 Parameters obtained from Rietveld refinement of the KVPO electrode charged to 4.8 V.

atom	Wyckoff site	*x*	*y*	*z*	*g*	*B*
V1	4*a*	0.3849(3)	0.4730(6)	0	1	0.5
V2	4*a*	0.2590(3)	0.2649(7)	0.2653(6)	1	0.5
P1	4*a*	0.5023(7)	0.3287(7)	0.2658(9)	1	1.0
P2	4*a*	0.1884(4)	0.4891(11)	0.5325(6)	1	1.0
K1	4*a*	0.420(4)	0.834(7)	0.392(5)	0.100(6)	1.5
K2	4*a*	0.0972(6)	0.6589(9)	0.0809(7)	= 0.91 – *g*(K1)	1.5
O1	4*a*	0.4877(13)	0.464(2)	0.1384(10)	1	1.0
O2	4*a*	0.5140(13)	0.513(2)	0.3813(11)	1	1.0
O3	4*a*	0.4030(11)	0.170(2)	0.2916(14)	1	1.0
O4	4*a*	0.5977(11)	0.201(2)	0.2570(14)	1	1.0
O5	4*a*	0.1112(12)	0.2848(18)	0.5466(13)	1	1.0
O6	4*a*	0.1181(11)	0.6725(18)	0.5028(14)	1	1.0
O7	4*a*	0.2482(9)	0.497(2)	0.6512(12)	1	1.0
O8	4*a*	0.2667(10)	0.432(2)	0.4160(16)	1	1.0
O9	4*a*	0.2730(11)	0.444(3)	0.1582(12)	1	1.0
O10	4*a*	0.2180(11)	0.029(2)	0.4045(14)	1	1.0

* The occupancy of K was fixed to be 0.91, which is presumed from reversible capacity of 72.5 mAh g^{-1} corresponding to the 0.545 potassiated state.

(a) KVPF



(b) KVPO

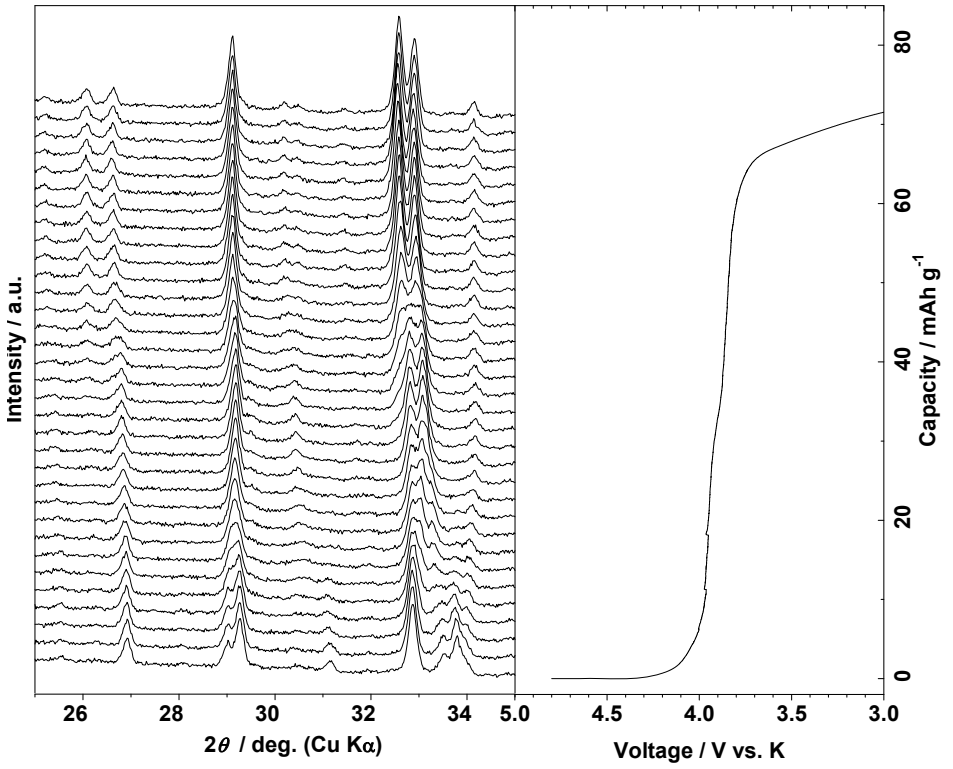


Figure S13 In-situ XRD patterns of (a) KVPF and (b) KVPO on the discharge process.

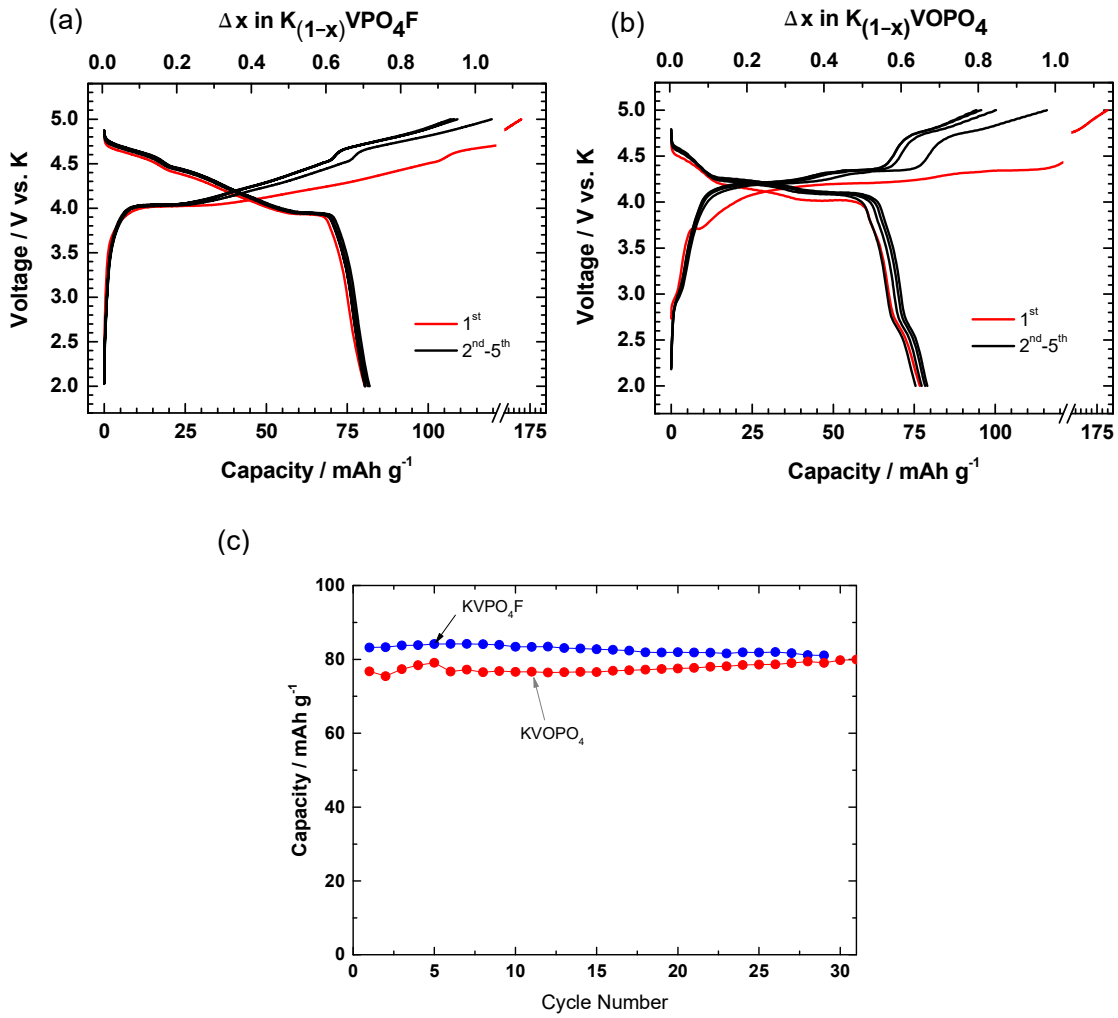


Figure S14 Charge and discharge profiles of (a) KVPF and (b) KVPO in K cells with 0.7 M/KPF_6 EC/DMC (1:1) in the voltage range of 5.0 – 2.0 V and (c) their cycle performance. Average discharge voltages of KVPF and KVPO are 4.13 and 4.02, respectively.

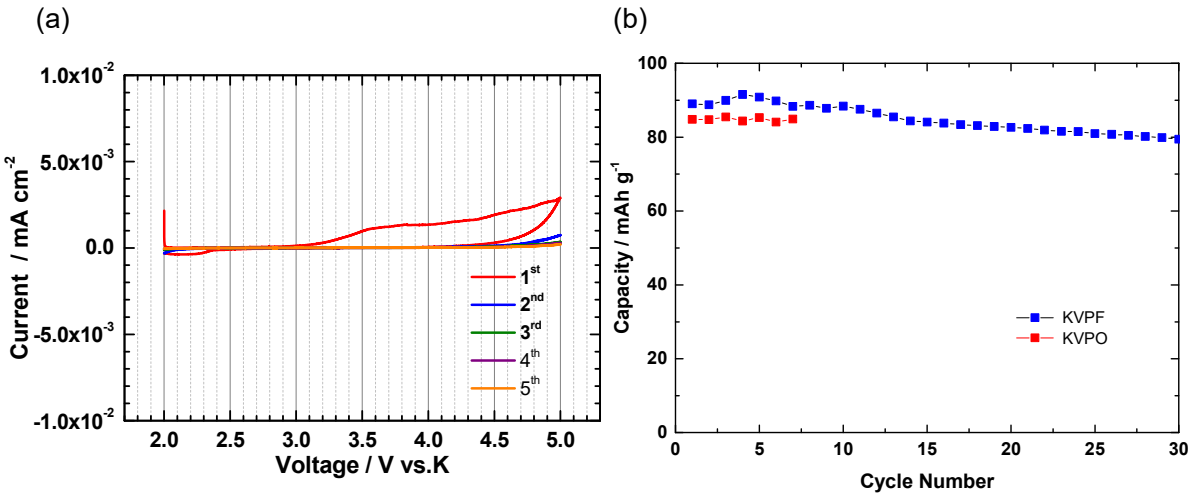


Figure S15 (a) CV curves of 1 M KPF_6 in EC:PC (1:1 v/v). 1 M KPF_6 EC/PC was prepared by dissolving KPF_6 in EC/PC mixture. A coin cell was assembled with Al foil as a working electrode against a metallic potassium counter electrode. Cyclic voltammetry measurement was carried out at a scanning speed of 0.5 mV s^{-1} in 2.0 – 5.0 V. (b) Cycle performances of KVPF and KVPO with 1 M/KPF_6 EC/PC (1:1 v/v) electrolyte. The discharge capacity reached to 92 mAh g^{-1} at 5^{th} cycle, however, the capacity was gradually decreasing with cycles.

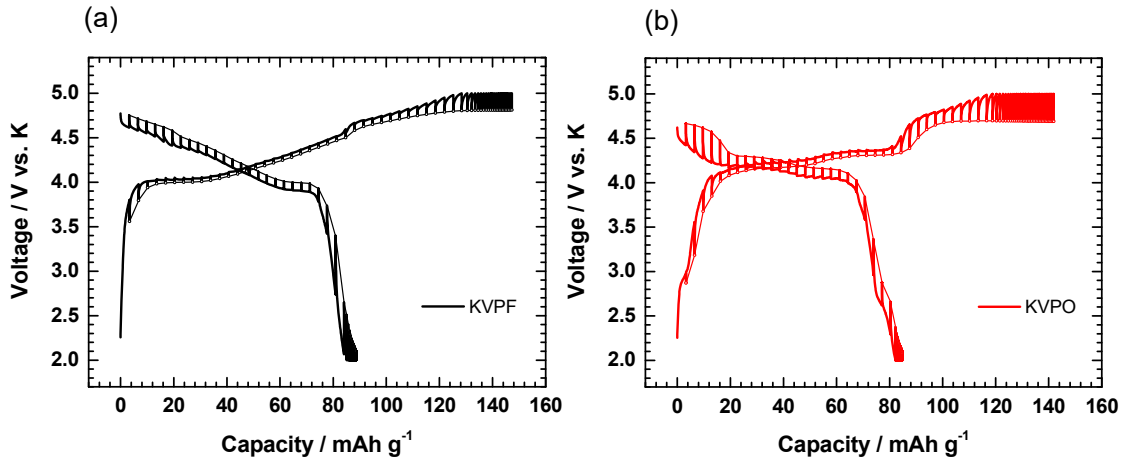


Figure S16 QOCV curve of (a) KVPF and (b) KVPO in 0.7 M KPF_6 EC/DEC (1:1 v/v) with the voltage range of 5.0 – 2.0 V. The cells was cycled with current density of C/20 in the 1st cycle, and then the current was curtailed at each 30 minutes with 1 h relaxation corresponding to an equivalent rate of C/80 for 1 electron reaction. Set of cycles was prolonged twice in order to monitor the behavior at upper voltage.

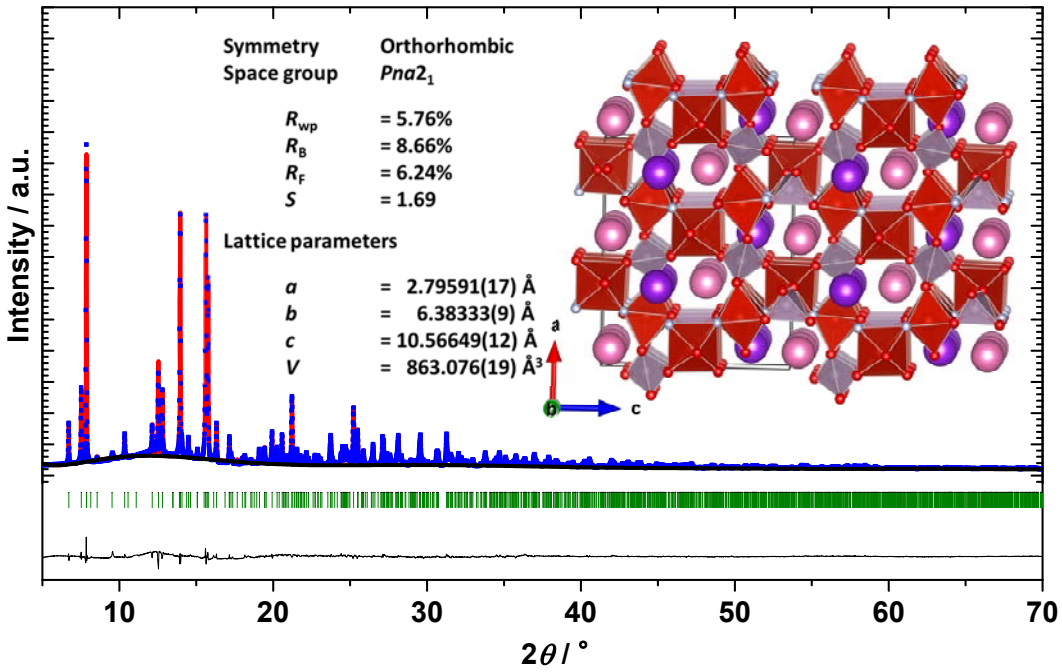


Figure S17 Result of Rietveld refinement for the KVPF electrode at the initial state. The blue dots and red lines represent experimental and calculated values, respectively. The black lines are the difference between the calculated and observed patterns and the vertical green bars correspond to the expected positions of Bragg reflections.

Table S3 Parameters obtained from Rietveld refinement of the KVPF electrode at the initial state.

atom	Wyckoff site	x	y	z	g	B
V1	4a	0.3831(2)	0.4929(9)	0	1	0.5
V2	4a	0.2472(5)	0.2528(9)	0.2500(13)	1	0.5
P1	4a	0.5002(9)	0.3318(7)	0.2520(15)	1	1.0
P2	4a	0.1829(4)	0.4988(16)	0.4979(14)	1	1.0
K1	4a	0.3809(5)	0.7822(8)	0.3082(9)	1	1.5
K2	4a	0.1052(5)	0.6980(7)	0.0632(9)	1	1.5
O1	4a	0.4815(16)	0.487(3)	0.1430(16)	1	1.0
O2	4a	0.5126(16)	0.484(3)	0.3787(15)	1	1.0
O3	4a	0.3982(13)	0.187(3)	0.283(2)	1	1.0
O4	4a	0.5931(13)	0.199(3)	0.230(2)	1	1.0
O5	4a	0.1058(15)	0.311(2)	0.533(2)	1	1.0
O6	4a	0.1173(13)	0.692(3)	0.478(2)	1	1.0
O7	4a	0.2535(18)	0.527(4)	0.6274(19)	1	1.0
O8	4a	0.249(2)	0.468(4)	0.386(2)	1	1.0
F1	4a	0.2681(12)	0.487(3)	0.1333(16)	1	1.0
F2	4a	0.2228(12)	0.056(2)	0.3803(15)	1	1.0

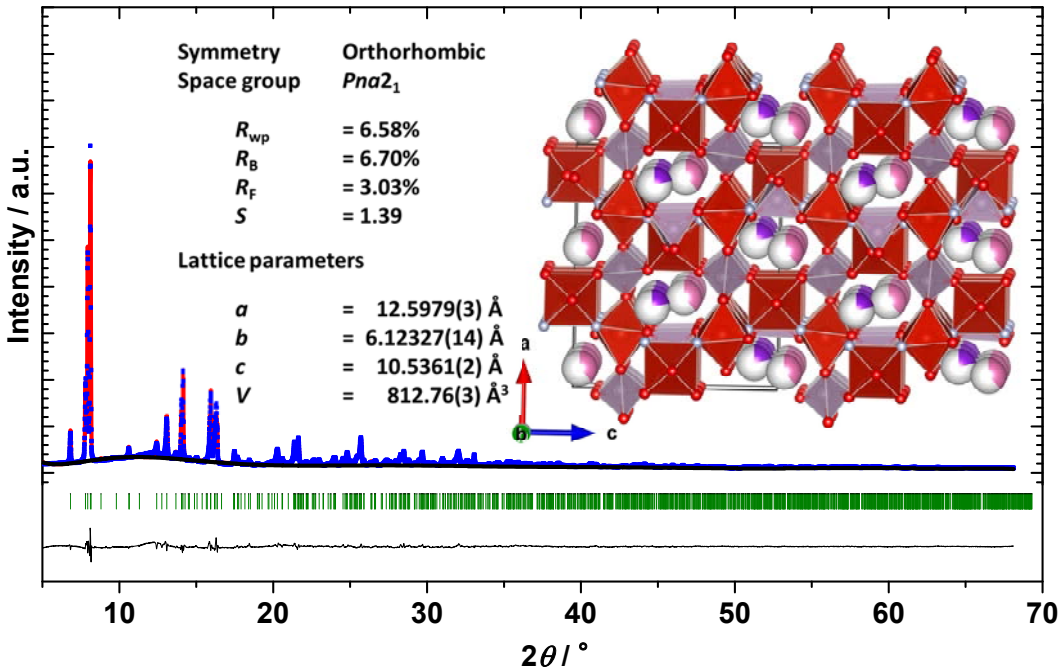


Figure S18 Result of Rietveld refinement for the KVPF electrode charged to 5.0 V. The blue dots and red lines represent experimental and calculated values, respectively. The black lines are the difference between the calculated and observed patterns and the vertical green bars correspond to the expected positions of Bragg reflections.

Table S4 Parameters obtained from Rietveld refinement of the KVPF electrode charged to 5.0 V.

atom	Wyckoff site	*x*	*y*	*z*	*g*	*B*
V1	4*a*	0.3994(4)	0.495(2)	0	1	0.5
V2	4*a*	0.2444(7)	0.2370(16)	0.2439(19)	1	0.5
P1	4*a*	0.5105(10)	0.3265(9)	0.243(3)	1	1
P2	4*a*	0.1899(6)	0.516(2)	0.499(2)	1	1.0
K1	4*a*	0.365(3)	0.831(7)	0.400(3)	0.215(18)*	1.5
K2	4*a*	0.105(2)	0.636(3)	0.050(2)	= 0.60 - *g*(K1)	1.5
O1	4*a*	0.489(3)	0.489(6)	0.125(5)	1	1.0
O2	4*a*	0.512(3)	0.483(6)	0.373(5)	1	1.0
O3	4*a*	0.396(2)	0.183(5)	0.266(3)	1	1.0
O4	4*a*	0.598(2)	0.180(5)	0.248(3)	1	1.0
O5	4*a*	0.110(3)	0.309(5)	0.508(3)	1	1.0
O6	4*a*	0.109(3)	0.701(6)	0.468(3)	1	1.0
O7	4*a*	0.264(4)	0.517(8)	0.619(3)	1	1.0
O8	4*a*	0.256(4)	0.468(6)	0.375(4)	1	1.0
F1	4*a*	0.276(3)	0.441(5)	0.125(4)	1	1.0
F2	4*a*	0.224(3)	0.028(7)	0.370(3)	1	1.0

* The occupancy of K was fixed to be 0.60, which is presumed from reversible capacity of 92 mAh g^{-1} corresponding to the 0.7 potassiated state.

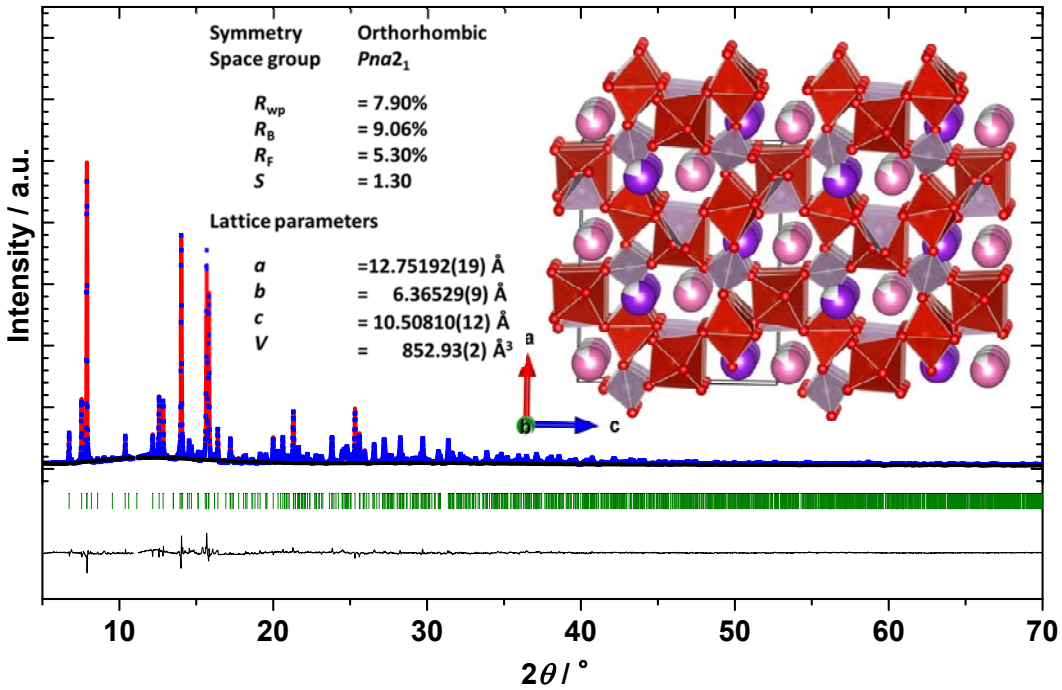


Figure S19 Result of Rietveld refinement for the KVPO electrode at the initial state. The blue dots and red lines represent experimental and calculated values, respectively. The black lines are the difference between the calculated and observed patterns and the vertical green bars correspond to the expected positions of Bragg reflections.

Table S5 Parameters obtained from Rietveld refinement of the KVPO electrode at the initial state.

atom	Wyckoff site	*x*	*y*	*z*	*g*	*B*
V1	4*a*	0.3778(2)	0.4869(8)	0	1	0.5
V2	4*a*	0.2471(5)	0.2700(6)	0.2570(9)	1	0.5
P1	4*a*	0.5004(8)	0.3297(8)	0.2621(12)	1	1.0
P2	4*a*	0.1817(4)	0.5083(13)	0.5181(8)	1	1.0
K1	4*a*	0.3840(6)	0.7872(11)	0.3194(9)	0.790(10)*	1.5
K2	4*a*	0.1069(6)	0.7048(10)	0.0759(9)	= 1.64 - *g*(K1)	1.5
O1	4*a*	0.4894(16)	0.483(2)	0.1435(14)	1	1.0
O2	4*a*	0.5211(13)	0.500(3)	0.3789(12)	1	1.0
O3	4*a*	0.3977(13)	0.193(3)	0.2923(17)	1	1.0
O4	4*a*	0.5942(12)	0.184(3)	0.243(2)	1	1.0
O5	4*a*	0.0983(14)	0.322(2)	0.5551(18)	1	1.0
O6	4*a*	0.1124(13)	0.693(2)	0.4886(19)	1	1.0
O7	4*a*	0.2479(12)	0.521(3)	0.6393(13)	1	1.0
O8	4*a*	0.2615(12)	0.454(3)	0.4086(17)	1	1.0
O9	4*a*	0.2546(11)	0.465(3)	0.1459(16)	1	1.0
O10	4*a*	0.2136(10)	0.024(3)	0.3947(16)	1	1.0

* The occupancy of K was fixed to be 1.64 based on the result from quantities analysis.

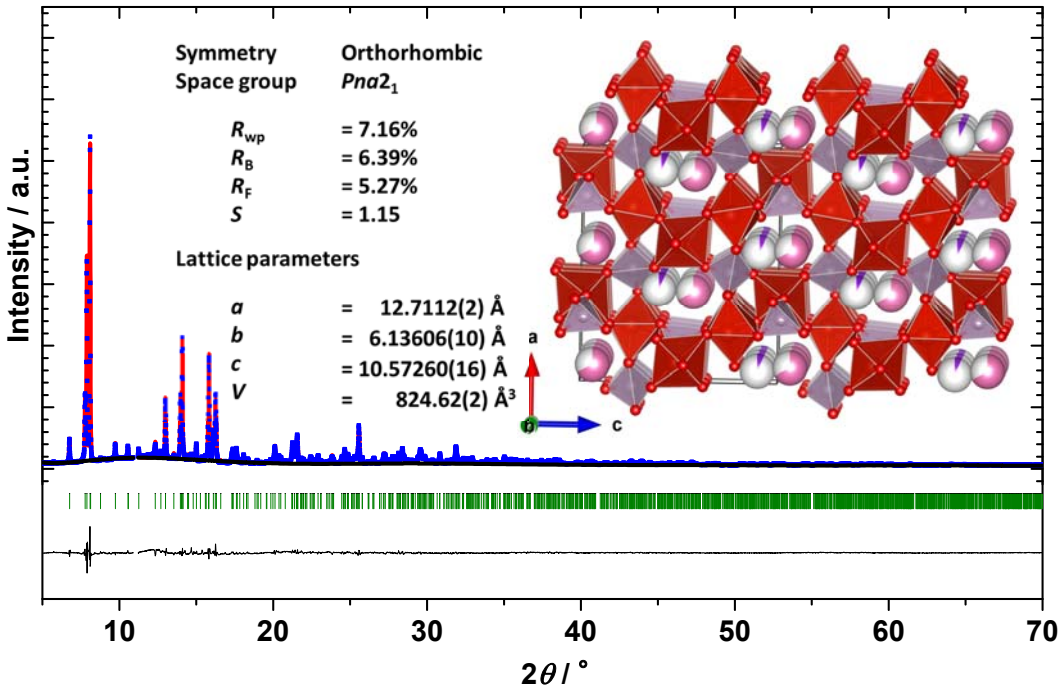


Figure S20 Result of Rietveld refinement for the KVPO electrode charged to 5.0 V. The blue dots and red lines represent experimental and calculated values, respectively. The black lines are the difference between the calculated and observed patterns and the vertical green bars correspond to the expected positions of Bragg reflections.

Table S6 Parameters obtained from Rietveld refinement of the KVPO electrode charged to 5.0 V.

Atom	Wyckoff site	*x*	*y*	*z*	*g*	*B*
V1	4*a*	0.3856(3)	0.4743(7)	0	1	0.5
V2	4*a*	0.2595(3)	0.2633(7)	0.2672(6)	1	0.5
P1	4*a*	0.5029(7)	0.3258(7)	0.2732(9)	1	1.0
P2	4*a*	0.1900(4)	0.4953(15)	0.5360(7)	1	1.0
K1	4*a*	0.424(6)	0.864(12)	0.413(8)	0.065(6)*	1.5
K2	4*a*	0.0969(7)	0.6594(11)	0.0813(9)	= 0.74 - *g*(K1)	1.5
O1	4*a*	0.4834(12)	0.465(2)	0.1440(12)	1	1.0
O2	4*a*	0.5108(14)	0.512(2)	0.3854(11)	1	1.0
O3	4*a*	0.4020(12)	0.172(2)	0.3004(14)	1	1.0
O4	4*a*	0.5986(11)	0.210(2)	0.2617(14)	1	1.0
O5	4*a*	0.1081(12)	0.294(2)	0.5456(16)	1	1.0
O6	4*a*	0.1175(12)	0.673(2)	0.4930(18)	1	1.0
O7	4*a*	0.2496(10)	0.498(3)	0.6518(14)	1	1.0
O8	4*a*	0.2681(11)	0.426(3)	0.4193(17)	1	1.0
O9	4*a*	0.2652(11)	0.442(3)	0.1601(13)	1	1.0
O10	4*a*	0.2134(11)	0.022(3)	0.4074(14)	1	1.0

* The occupancy of K was fixed to be 0.74, which is presumed from reversible capacity of 84 mAh g^{-1} corresponding to the 0.63 potassiated state.