

Controlling the Cathodic Potential of KVPO₄F through Oxygen Substitution

Romain Wernert^{a,b,c}, Long H. B. Nguyen^{a,c}, Emmanuel Petit^{a,c}, Paula Sanz Camacho^a, Antonella Iadecola^c, Alessandro Longo^{d,e}, François Fauth^f, Lorenzo Stievano^{b,c,g}, Laure Monconduit^{b,c,g}, Dany Carlier^{a,c,g}, Laurence Croguennec^{a,c,g,*}

AUTHOR ADDRESS

^a Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

^b ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

^c RS2E, Réseau sur le Stockage Electrochimique de l'Energie, FR CNRS 3459, Amiens F-80039 Cedex 1, France

^d European Synchrotron Radiation Facility, 71, Avenue des Martyrs, Grenoble, F-38000, France

^e Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, UOS Palermo via Ugo La Malfa 153 90146, Italy

^f CELLS-ALBA synchrotron, E-08290, Cerdanyola del Vallès, Barcelona, Spain

^g ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France

* Email: Laurence.Croguennec@icmcb.cnrs.fr

Supplementary information

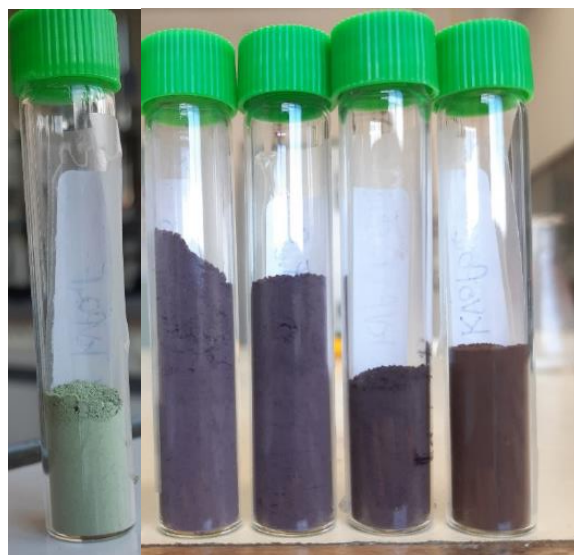


Figure S1: Photograph of the compounds $\text{KVPO}_4\text{F}_{1-y}\text{O}_y$ ($y = 0, 0.25, 0.5, 0.75, 1$), their color changes from green for $\text{KV}^{3+}\text{PO}_4\text{F}$ (left) to brown for $\text{KV}^{4+}\text{OPO}_4$ (right).

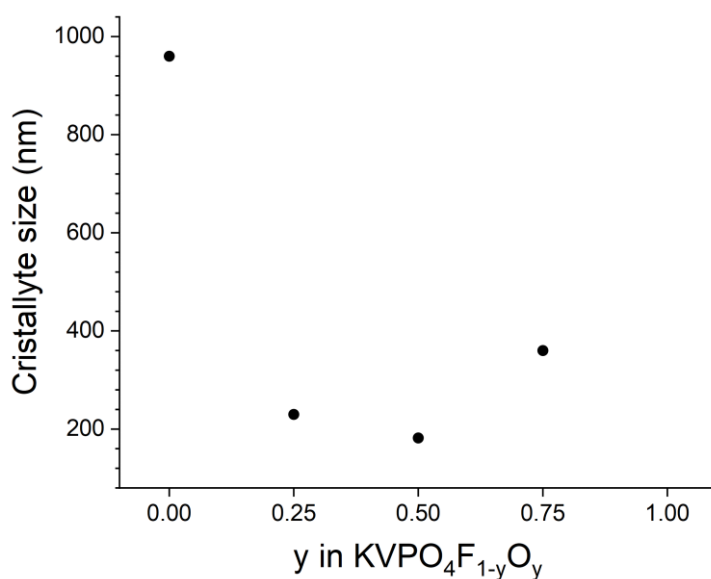


Figure S2: Variation of the crystallite size calculated with Scherrer law, averaged on (110), (212) and (512) Bragg peaks for $\text{KVPO}_4\text{F}_{1-y}\text{O}_y$. For KVOPO_4 there was no significant line broadening as compared to the instrumental resolution function, which suggests micrometre sized crystallites.

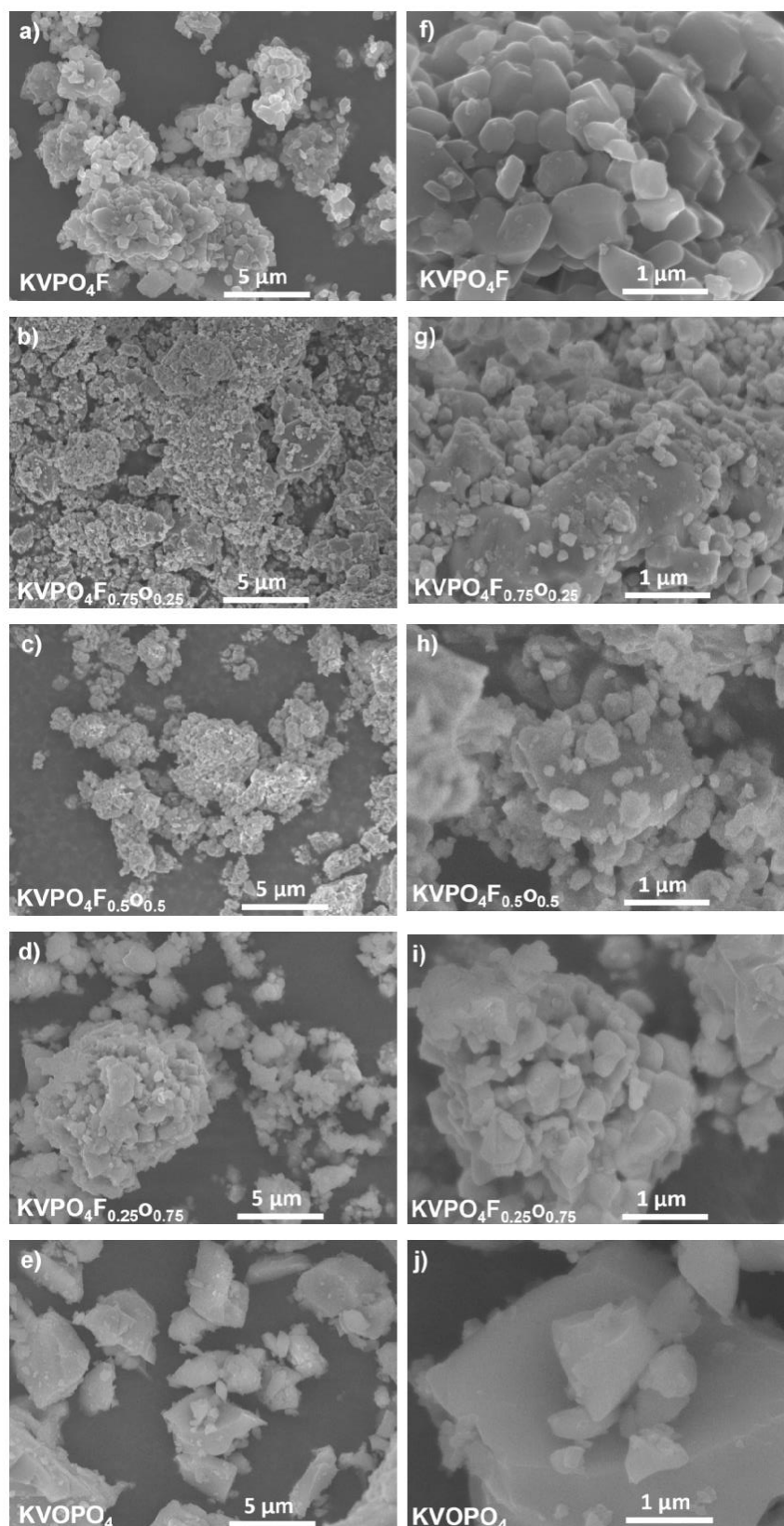


Figure S3: SEM images of $\text{KVPO}_4\text{F}_{1-y}\text{O}_y$ at x5000 (a-e) and x25000 (f-j) magnifications

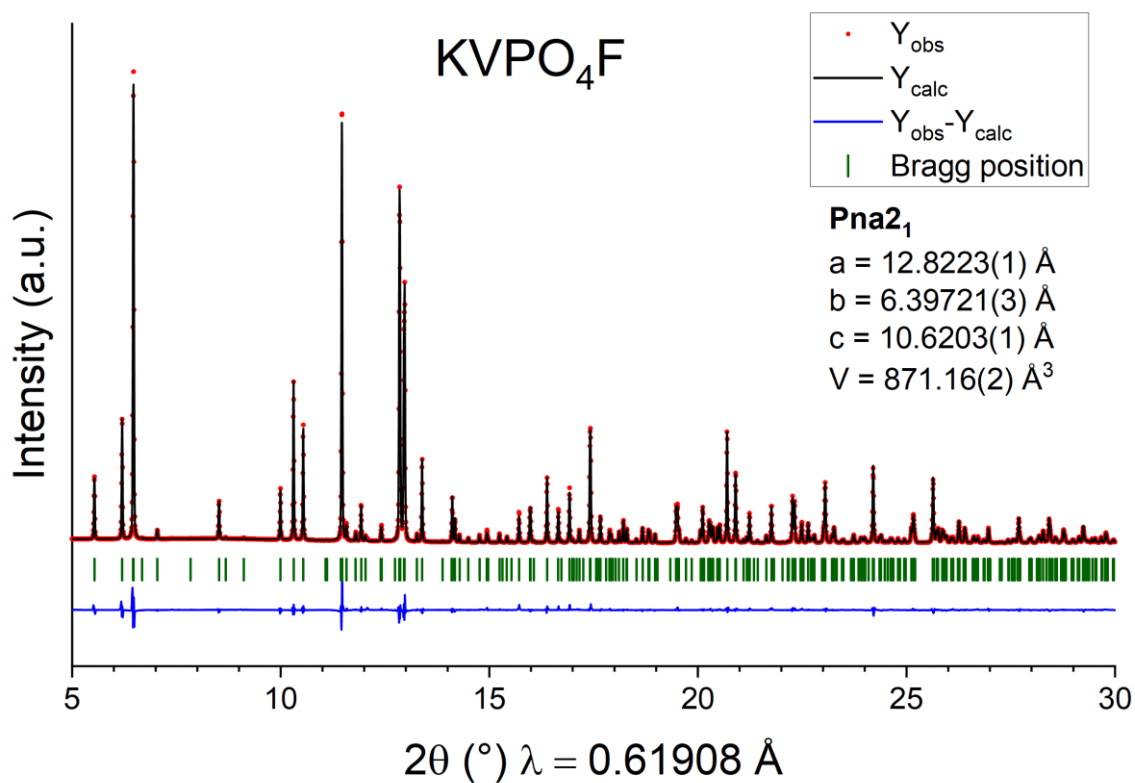


Figure S4: Rietveld refinement of the SXRD pattern of KVPO₄F. $R_p=3.06\%$; $R_{wp}=4.46\%$; $\chi^2=9.14$.

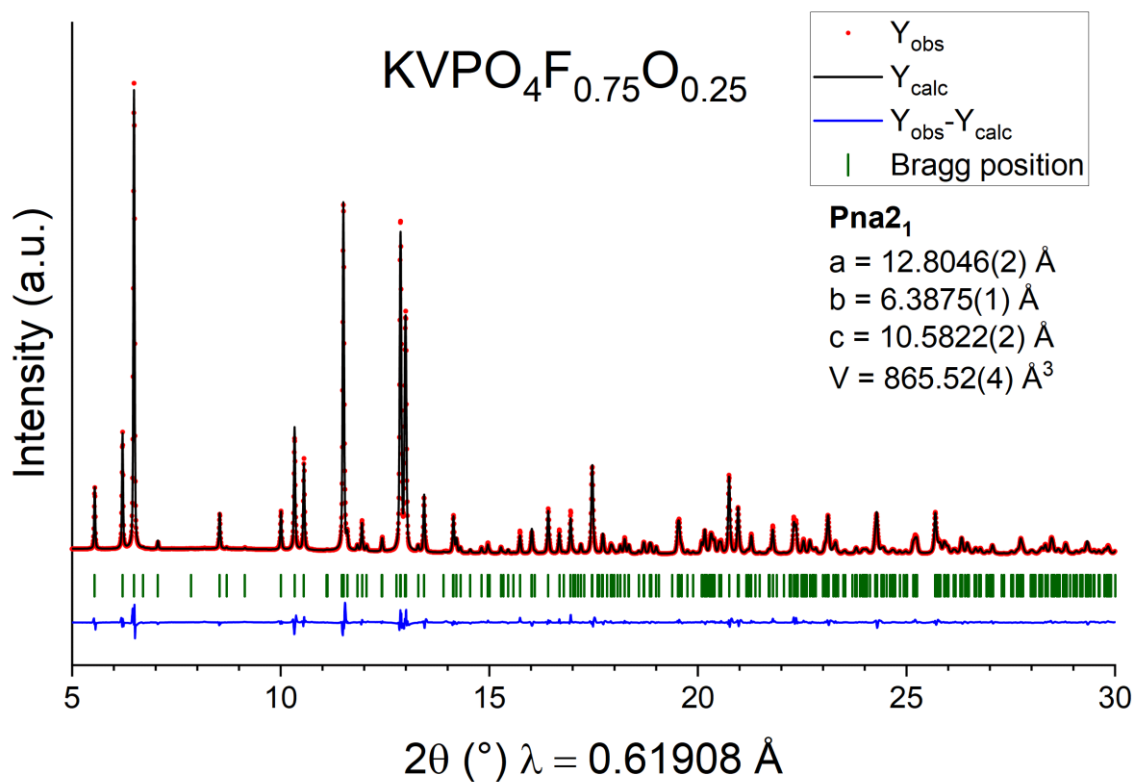


Figure S5: Rietveld refinement of the SXRD pattern of KVPO₄F_{0.75}O_{0.25}. $R_p=3.76\%$; $R_{wp}=5.22\%$; $\chi^2=10.72$.

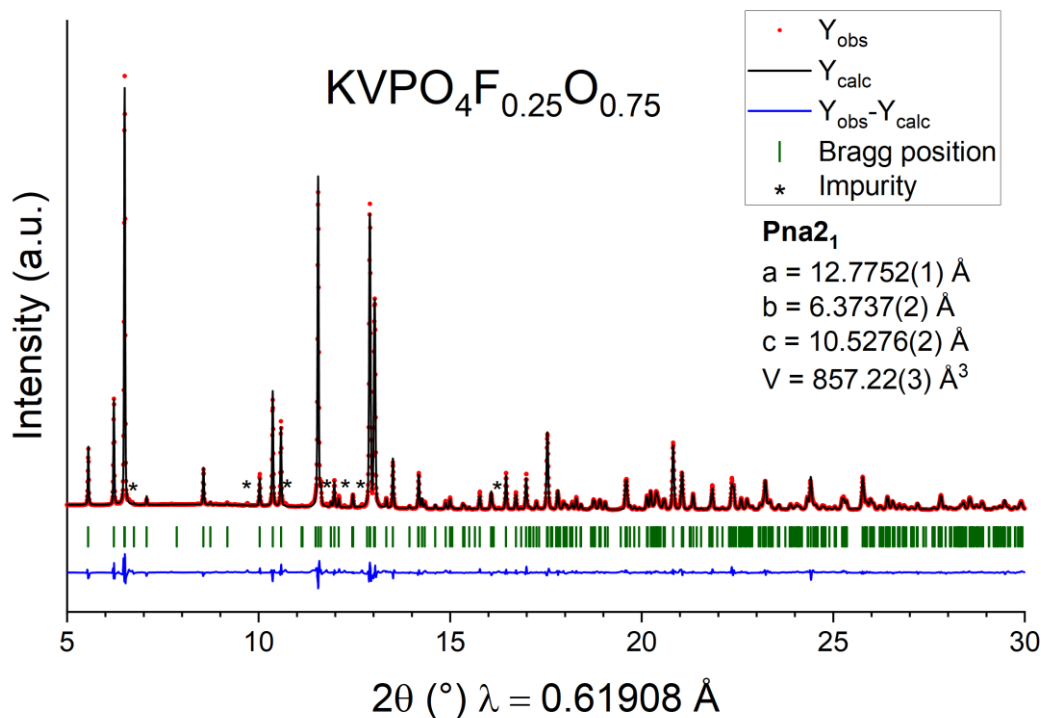


Figure S6: Rietveld refinement of the SXRD pattern of KVPO₄F_{0.25}O_{0.75}. $R_p=4.22\%$; $R_{wp}=5.85\%$; $\chi^2=11.49$.

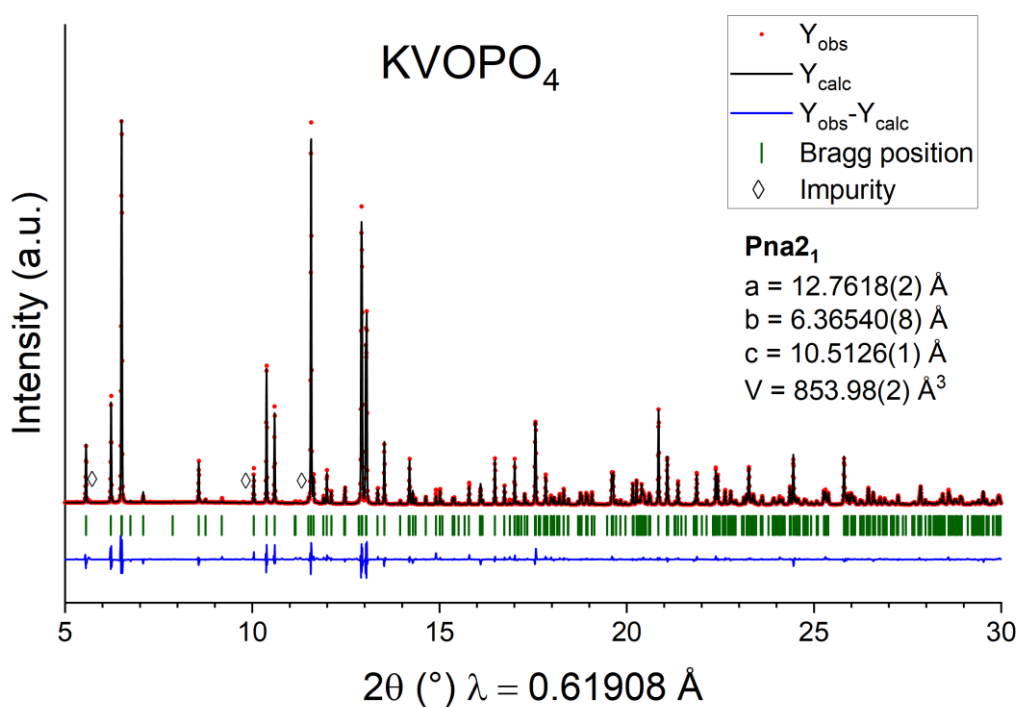


Figure S7: Rietveld refinement of the SXRD pattern of KVOPO₄. This particular sample is more crystalline (due to a higher annealing temperature, 750°C versus 650°C for the others) and hence the peaks are very sharp compared to the angular resolution which affects the quality of the profile matching. $R_p=5.17\%$; $R_{wp}=7.81\%$; $\chi^2=17.34$.

Table S1: cell parameters and unit cell volume per formula unit derived from Rietveld refinements.

	a (Å)	b (Å)	c (Å)	V/Z (Å ³)
KVPO ₄ F	12.8223(1)	6.39721(3)	10.6203(1)	108.90(1)
KVPO ₄ F _{0.75} O _{0.25}	12.8046(5)	6.3875(2)	10.5822(3)	108.19(1)
KVPO ₄ F _{0.5} O _{0.5}	12.7912(2)	6.3819(2)	10.5456(2)	107.60(2)
KVPO ₄ F _{0.25} O _{0.75}	12.7752(1)	6.3737(2)	10.5276(2)	107.15(2)
KVOPO ₄	12.7618(2)	6.36540(8)	10.5126(1)	106.74(2)

Table S2: Atomic parameters and first neighbour interatomic distances of KVPO₄F refined by the Rietveld method.

KVPO ₄ F		Pna2 ₁		Z=8	ρ=3.11 g/cm ³	
		a (Å)	b (Å)	c (Å)		
		12.8223(1)	6.39721(3)	10.6203(1)		
	Pos	x/a	y/b	z/c	occupancy	B _{iso} (Å ²)
K1	4a	0.3802(1)	0.7788(2)	0.30175(2)	1.02(2)	1.87(3)
K2	4a	0.1044(1)	0.6972(2)	0.0590(2)	0.97(2)	1.88(3)
V1	4a	0.3854(7)	0.4967(2)	0	1	0.47(1)
V2	4a	0.2469(1)	0.2514(2)	0.2469(2)	1	0.45(1)
P1	4a	0.4988(2)	0.3311(2)	0.2501(3)	1	0.50(1)
P2	4a	0.1817(1)	0.4991(4)	0.4991(3)	1	0.50(1)
O1	4a	0.4848(4)	0.4865(6)	0.1406(3)	1	0.44(2)
O2	4a	0.5122(4)	0.4682(6)	0.3691(3)	1	0.44(2)
O3	4a	0.4008(3)	0.1959(3)	0.2689(3)	1	0.44(2)
O4	4a	0.5955(3)	0.1935(6)	0.2286(5)	1	0.44(2)
O5	4a	0.1112(3)	0.3107(5)	0.5292(4)	1	0.44(2)
O6	4a	0.1127(3)	0.6910(5)	0.4722(4)	1	0.44(2)
O7	4a	0.2501(4)	0.5377(9)	0.6163(4)	1	0.44(2)
O8	4a	0.2566(4)	0.458(1)	0.3888(4)	1	0.44(2)
F1	4a	0.2706(4)	0.523(1)	0.8788(4)	1	0.71(4)
F2	4a	0.2716(4)	0.4777(9)	0.1266(4)	1	0.71(4)

Bond	Distance (Å)*	Bond	Distance (Å)*
V1-O1	1.961	V2-O3	2.018
V1-O2	1.928	V2-O4	1.983
V1-O5	2.032	V2-O7	1.948
V1-O6	1.979	V2-O8	2.011
V1-F1	1.965	V2-F1	2.034
V1-F2	1.984	V2-F2	1.957
P1-O1	1.541	P2-O5	1.540
P1-O2	1.548	P2-O6	1.540
P1-O3	1.538	P2-O7	1.540
P1-O4	1.537	P2-O8	1.537

	Minimum distance (Å)*	Average distance (Å)*	Maximum distance (Å)*
K1-O/F	2.617	2.830	3.069
K2-O/F	2.661	2.932	3.083
	V1(O ₄ F ₂)	V2(O ₄ F ₂)	
Site distortion (10 ⁻⁴)	2.50	3.33	

*Rounded to 10⁻³ Å

The site distortion depicts the deviation from a regular octahedron and was calculated using the following formula:

$$\Delta = \frac{1}{6} \sum_{i=1}^6 \frac{(d_i - \bar{d})^2}{\bar{d}^2}$$

Where d_i corresponds to each V-X bond of the octahedron and \bar{d} is the average bond length.

Table S3: Atomic parameters and first neighbour interatomic distances of KVPO₄F_{0.75}O_{0.25} refined by the Rietveld method.

KVPO ₄ F _{0.75} O _{0.25}		Pna2 ₁		Z=8	ρ=3.13 g/cm ³	
		a (Å)	b (Å)	c (Å)		
		12.8046(5)	6.3875(2)	10.5822(3)		
	Pos	x/a	y/b	z/c	occupancy	B _{iso} (Å ²)
K1	4a	0.381(1)	0.779(1)	0.304(1)	1.02(4)	2.2(3)
K2	4a	0.104(1)	0.699(1)	0.061(2)	0.95(4)	2.3(3)
V1	4a	0.3830(5)	0.497(2)	0	1	0.9(1)
V2	4a	0.247(1)	0.254(1)	0.245(1)	1	0.9(1)
P1	4a	0.497(1)	0.331(1)	0.250(2)	1	0.8(1)
P2	4a	0.1811(5)	0.498(3)	0.499(2)	1	0.8(1)
O1	4a	0.483(3)	0.486(5)	0.140(2)	1	0.5(1)
O2	4a	0.510(3)	0.467(5)	0.370(2)	1	0.5(1)
O3	4a	0.399(2)	0.196(5)	0.272(4)	1	0.5(1)
O4	4a	0.594(2)	0.193(5)	0.229(3)	1	0.5(1)
O5	4a	0.110(2)	0.311(4)	0.534(3)	1	0.5(1)
O6	4a	0.110(2)	0.688(4)	0.472(3)	1	0.5(1)
O7	4a	0.250(3)	0.534(5)	0.616(2)	1	0.5(1)
O8	4a	0.255(3)	0.457(5)	0.388(2)	1	0.5(1)
X1	4a	0.275(3)	0.528(5)	0.880(2)	1	1.5(3)
X2	4a	0.270(3)	0.475(5)	0.126(3)	1	1.5(3)

Bond	Distance (Å)*	Bond	Distance (Å)*
V1-O1	1.964	V2-O3	1.998
V1-O2	1.944	V2-O4	2.002
V1-O5	2.046	V2-O7	1.957
V1-O6	1.993	V2-O8	1.996
V1-X1	1.884	V2-X1	2.054
V1-X2	1.972	V2-X2	1.908
P1-O1	1.540	P2-O5	1.540
P1-O2	1.547	P2-O6	1.538
P1-O3	1.536	P2-O7	1.537
P1-O4	1.540	P2-O8	1.540
	Minimum distance (Å)*	Average distance (Å)*	Maximum distance (Å)*
K1-O/F	2.678	2.831	3.071
K2-O/F	2.664	2.924	3.078
	V1(O ₄ X ₂)	V2(O ₄ X ₂)	
Site distortion (10 ⁻⁴)	6.29	5.40	

*Rounded to 10⁻³ Å

Table S4: Atomic parameters and first neighbour interatomic distances of KVPO₄F_{0.5}O_{0.5} refined by the Rietveld method.

KVPO ₄ F _{0.5} O _{0.5}		Pna2 ₁		Z=8	ρ=3.15 g/cm ³	
		a (Å)	b (Å)	c (Å)		
		12.7912(2)	6.3819(2)	10.5456(2)		
	Pos	x/a	y/b	z/c	occupancy	B _{iso} (Å ²)
K1	4a	0.381(1)	0.779(1)	0.306(2)	1.02(4)	2.3(5)
K2	4a	0.103(1)	0.701(2)	0.059(2)	0.96(4)	2.4(5)
V1	4a	0.3806(6)	0.496(2)	0	1	1.1(2)
V2	4a	0.247(1)	0.258(2)	0.242(1)	1	1.1(1)
P1	4a	0.498(2)	0.330(1)	0.248(2)	1	0.8(1)
P2	4a	0.1797(6)	0.498(3)	0.500(2)	1	0.8(1)
O1	4a	0.482(3)	0.487(5)	0.138(2)	1	0.5(1)
O2	4a	0.510(3)	0.467(5)	0.368(2)	1	0.5(1)
O3	4a	0.400(2)	0.196(4)	0.272(4)	1	0.5(1)
O4	4a	0.594(2)	0.190(4)	0.230(4)	1	0.5(1)
O5	4a	0.109(2)	0.309(4)	0.531(3)	1	0.5(1)
O6	4a	0.110(2)	0.690(4)	0.471(3)	1	0.5(1)
O7	4a	0.251(3)	0.532(6)	0.616(3)	1	0.5(1)
O8	4a	0.254(6)	0.454(6)	0.388(3)	1	0.5(1)
X1	4a	0.279(3)	0.528(6)	0.879(3)	1	2.3(4)
X2	4a	0.268(3)	0.469(6)	0.128(3)	1	2.3(4)

Bond	Distance (Å)*	Bond	Distance (Å)*
V1-O1	1.964	V2-O3	2.016
V1-O2	1.972	V2-O4	1.986
V1-O5	2.029	V2-O7	1.966
V1-O6	1.979	V2-O8	1.986
V1-X1	1.822	V2-X1	2.086
V1-X2	1.981	V2-X2	1.825
P1-O1	1.541	P2-O5	1.537
P1-O2	1.549	P2-O6	1.537
P1-O3	1.539	P2-O7	1.541
P1-O4	1.536	P2-O8	1.541

	Minimum distance (Å)*	Average distance (Å)*	Maximum distance (Å)*
K1-O/F	2.670	2.852	3.086
K2-O/F	2.647	2.890	3.085

	V1(O ₄ X ₂)	V2(O ₄ X ₂)
Site distortion (10 ⁻⁴)	11.3	15.7

*Rounded to 10⁻³ Å

	U ₁₁ (Å ²)	U ₂₂ (Å ²)	U ₃₃ (Å ²)	U ₁₂ (Å ²)	U ₂₃ (Å ²)	U ₁₃ (Å ²)
V1	0.013700	0.010950	0.017620	-0.001950	0.003190	-0.002670
V2	0.008890	0.019000	0.015880	0.000640	-0.004030	-0.000780
X1	0.013900	0.058630	0.019720	0.003530	0.013520	0.001080
X2	0.016620	0.013430	0.048770	0.003750	-0.006750	0.004770

Table S5: Atomic parameters and first neighbour interatomic distances of KVPO₄F_{0.25}O_{0.75} refined by the Rietveld method.

KVPO ₄ F _{0.25} O _{0.75}		Pna2 ₁		Z=8	ρ=3.16 g/cm ³	
		a (Å)	b (Å)	c (Å)		
		12.7752(1)	6.3737(2)	10.5276(2)		
	Pos	x/a	y/b	z/c	occupancy	B _{iso} (Å ²)
K1	4a	0.382(1)	0.782(1)	0.308(1)	1.02(4)	1.9(2)
K2	4a	0.1039(8)	0.702(1)	0.062(1)	0.95(3)	2.2(2)
V1	4a	0.3787(4)	0.495(2)	0	1	1.1(2)
V2	4a	0.2474(8)	0.266(1)	0.2431(8)	1	0.9(2)
P1	4a	0.497(1)	0.330(1)	0.248(2)	1	0.8(1)
P2	4a	0.1806(4)	0.497(2)	0.503(2)	1	0.8(1)
O1	4a	0.483(2)	0.485(4)	0.138(2)	1	0.4(1)
O2	4a	0.511(2)	0.464(4)	0.369(2)	1	0.4(1)
O3	4a	0.398(2)	0.197(4)	0.275(3)	1	0.4(1)
O4	4a	0.594(1)	0.188(4)	0.232(3)	1	0.4(1)
O5	4a	0.232(2)	0.309(3)	0.532(2)	1	0.4(1)
O6	4a	0.111(2)	0.689(3)	0.475(3)	1	0.4(1)
O7	4a	0.251(2)	0.532(4)	0.620(2)	1	0.4(1)
O8	4a	0.257(2)	0.451(4)	0.394(2)	1	0.4(1)
X1	4a	0.285(2)	0.514(4)	0.881(2)	1	2.7(4)
X2	4a	0.267(2)	0.460(4)	0.130(2)	1	2.7(4)

Bond	Distance (Å)*	Bond	Distance (Å)*
V1-O1	1.981	V2-O3	2.012
V1-O2	1.978	V2-O4	1.984
V1-O5	2.033	V2-O7	1.977
V1-O6	1.977	V2-O8	1.988
V1-X1	1.728	V2-X1	2.213
V1-X2	1.991	V2-X2	1.735
P1-O1	1.536	P2-O5	1.540
P1-O2	1.543	P2-O6	1.541
P1-O3	1.540	P2-O7	1.537
P1-O4	1.542	P2-O8	1.540

	Minimum distance (Å)*	Average distance (Å)*	Maximum distance (Å)*
K1-O/F	2.675	2.823	3.064
K2-O/F	2.637	2.874	3.073
	V1(O ₄ X ₂)	V2(O ₄ X ₂)	
Site distortion (10 ⁻⁴)	27.6	49.5	

*Rounded to 10⁻³ Å

Table S6: Atomic parameters and first neighbour interatomic distances of KVOPO₄ refined by the Rietveld method.

KVOPO ₄		Pna2 ₁		Z=8	ρ=3.17 g/cm ³	
		a (Å)	b (Å)	c (Å)		
		12.7618(2)	6.36540(8)	10.5126(1)		
	Pos	x/a	y/b	z/c	occupancy	B _{iso} (Å ²)
K1	4a	0.3820(3)	0.3820(3)	0.7827(9)	1.04(2)	1.4(1)
K2	4a	0.103(3)	0.7047(9)	0.0596(6)	0.96(2)	1.7(1)
V1	4a	0.3765(3)	0.4960(9)	0	1	0.74(6)
V2	4a	0.2478(4)	0.2739(6)	0.239(3)	1	0.40(8)
P1	4a	0.4961(6)	0.3307(6)	0.2490(9)	1	0.49(6)
P2	4a	0.1805(3)	0.498(6)	0.5052(3)	1	0.49(6)
O1	4a	0.483(1)	0.482(2)	0.136(1)	1	0.39(9)
O2	4a	0.512(1)	0.468(2)	0.368(1)	1	0.39(9)
O3	4a	0.3995(9)	0.191(3)	0.272(1)	1	0.39(9)
O4	4a	0.5936(6)	0.190(2)	0.233(2)	1	0.39(9)
O5	4a	0.110(1)	0.306(2)	0.529(1)	1	0.39(9)
O6	4a	0.109(1)	0.686(2)	0.474(1)	1	0.39(9)
O7	4a	0.250(1)	0.537(3)	0.621(1)	1	0.39(9)
O8	4a	0.257(1)	0.459(3)	0.394(1)	1	0.39(9)
O9	4a	0.287(1)	0.528(3)	0.882(2)	1	2.5(3)
O10	4a	0.268(2)	0.463(2)	0.132(2)	1	2.5(3)

Bond	Distance (Å)*	Bond	Distance (Å)*
V1-O1	1.994	V2-O3	2.036
V1-O2	1.985	V2-O4	1.982
V1-O5	2.008	V2-O7	1.943
V1-O6	1.994	V2-O8	2.023
V1-O9	1.683	V2-O9	2.215
V1-O10	1.981	V2-O10	1.666
P1-O1	1.535	P2-O5	1.539
P1-O2	1.545	P2-O6	1.538
P1-O3	1.540	P2-O7	1.538
P1-O4	1.540	P2-O8	1.540
	Minimum distance (Å)*	Average distance (Å)*	Maximum distance (Å)*
K1-O/F	2.677	2.859	3.104
K2-O/F	2.634	2.888	3.111
	V1(O ₄ X ₂)	V2(O ₄ X ₂)	
Site distortion (10 ⁻⁴)	37.2	68.4	

*Rounded to 10⁻³ Å

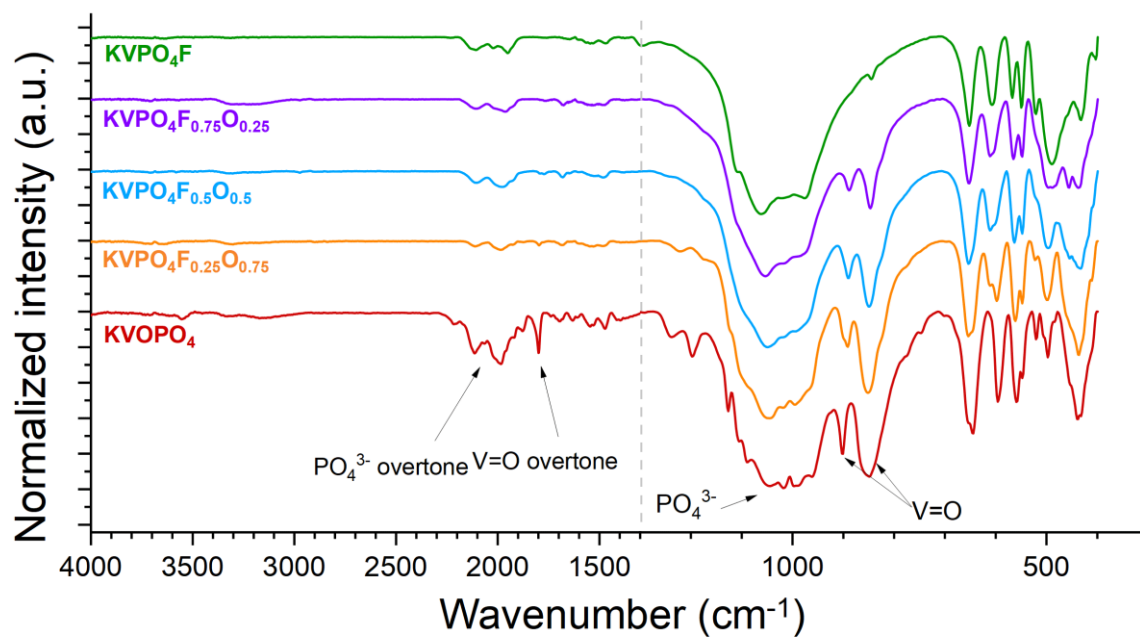


Figure S8: Fourier transformed infrared spectroscopy of the series of samples $\text{KVPO}_4\text{F}_{1-y}\text{O}_y$.

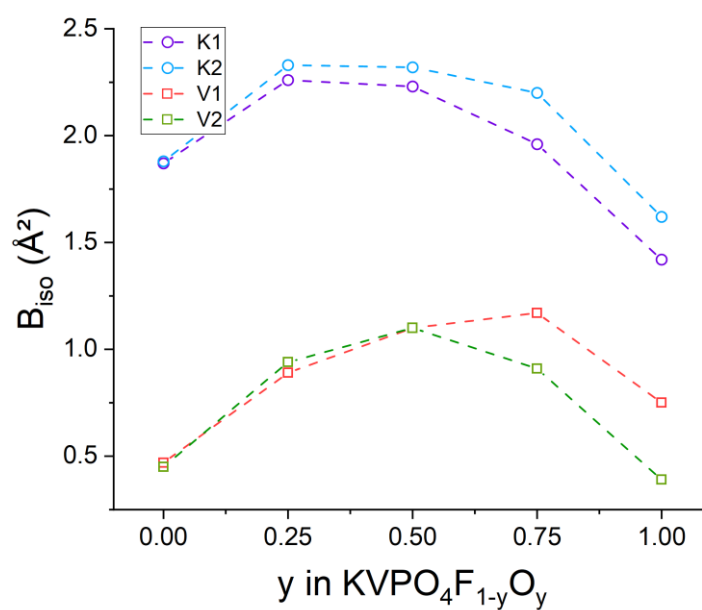


Figure S9: Variation of the $B_{\text{isotropic}}$ atomic displacement parameters determined for the different potassium and vanadium atoms

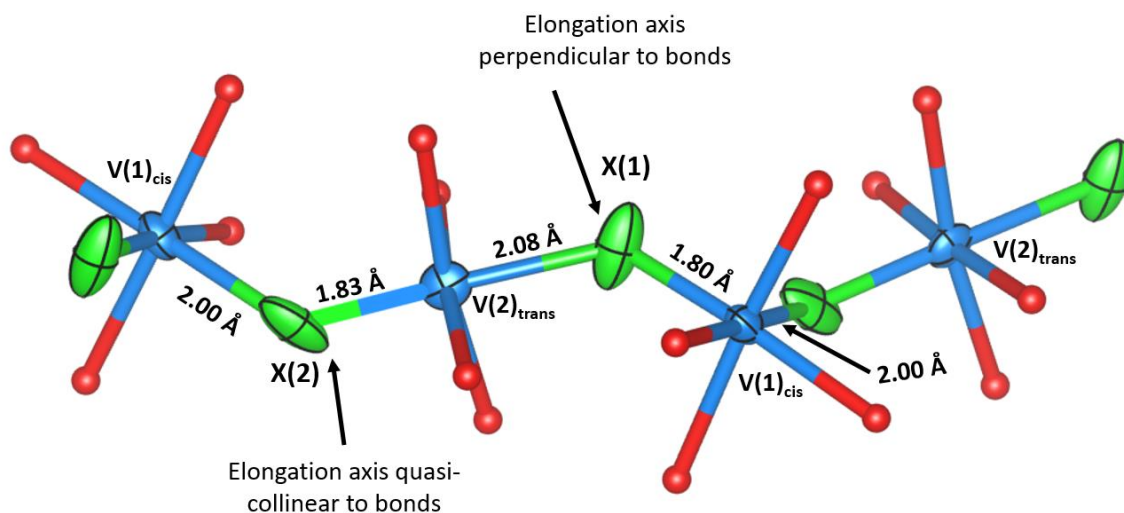


Figure S10: Drawing of the VO₄X₂ chain in KVPO₄F_{0.5}O_{0.5} displayed with atomic displacement parameter showing 80 % probability. The ellipsoid denotes that the positional disorder of X sites is far more important than that of V sites.

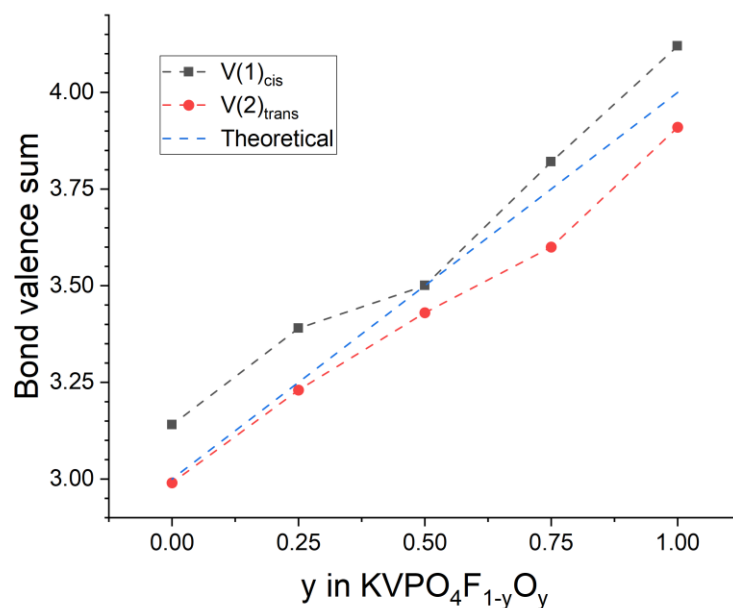


Figure S11: Bond valence sum calculated for V(1)_{cis} and V(2)_{trans} as function of the anionic composition, and compared to the theoretical vanadium average oxidation state.

Bond valence sums were calculated with the following formula:

$$BVS = \sum_{R_{exp}=1}^6 e^{\frac{R_0 - R_{exp}}{b}}$$

With parameters $b=0.37 \text{ \AA}$, $R_0(\text{V}^{\text{IV}}-\text{O})=1.78 \text{ \AA}$, $R_0(\text{V}^{\text{III}}-\text{O})=1.75 \text{ \AA}$, $R_0(\text{V}^{\text{III}}-\text{F})=1.70 \text{ \AA}$.

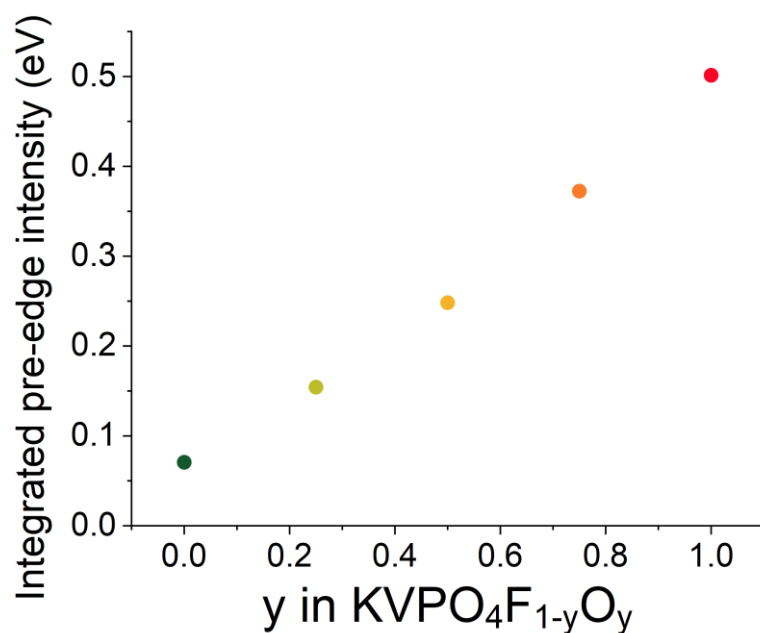


Figure S12: Integrated XANES pre-edge intensity plotted as function of the anionic stoichiometry in KVPO₄F_{1-y}O_y.

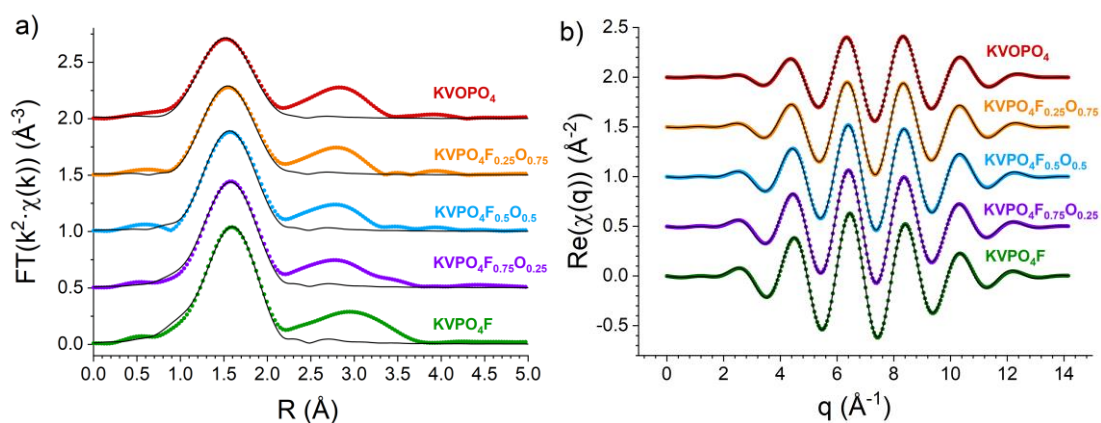


Figure S13: a) Fourier transforms of the k^2 weighted EXAFS oscillations for KVPO₄F_{1-y}O_y, fits of the first coordination shell are shown as black lines and compared to the experimental data as colored points; b) Corresponding back Fourier transformed EXAFS oscillations in the q space.

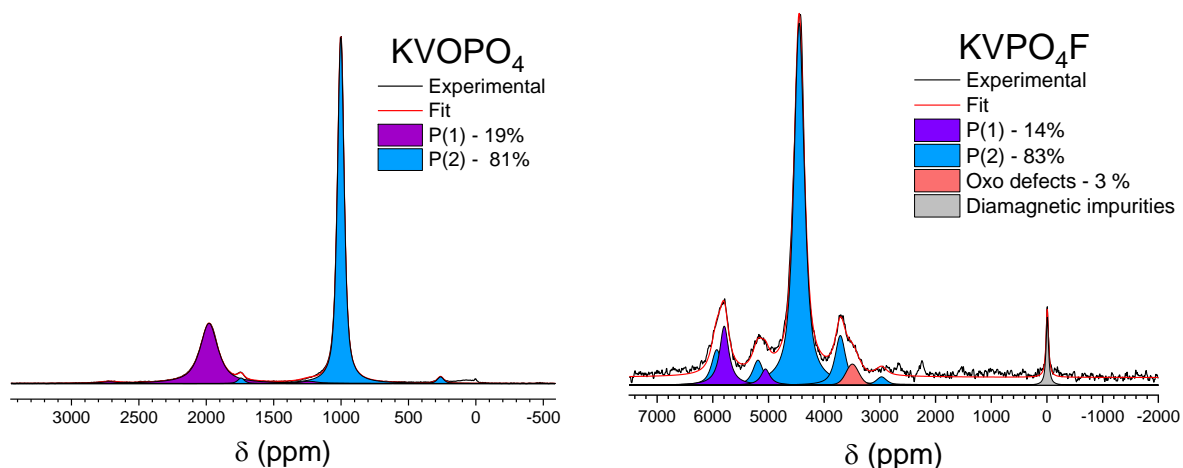


Figure S14: Experimental ^{31}P MAS NMR spectra of KVOPO_4 and KVPO_4F with desommatation of the different P environments, including spinning sidebands.

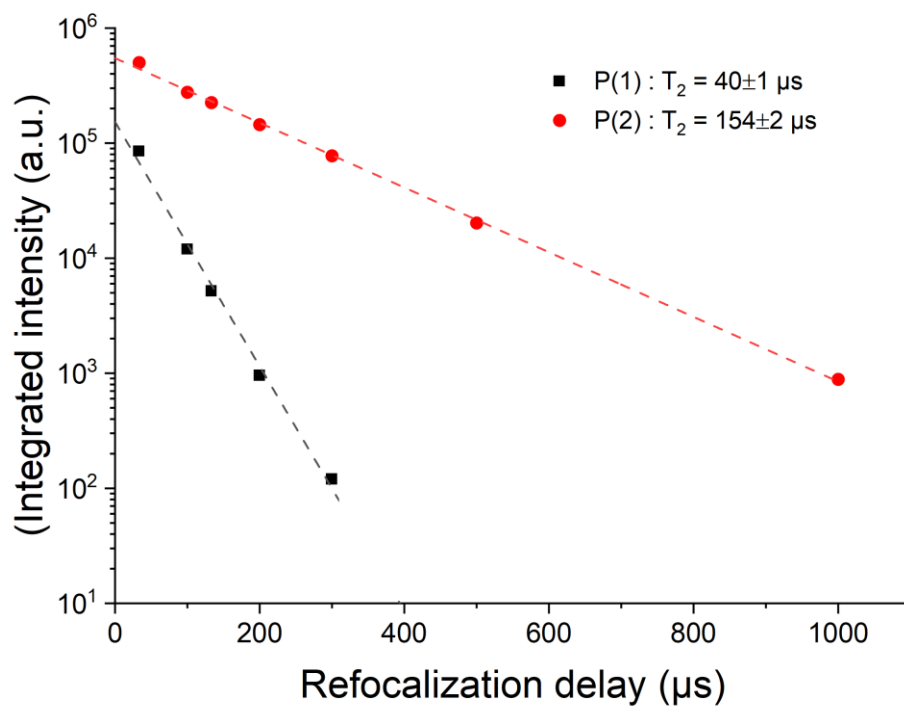


Figure S15: Semi-log plot of the integrated NMR peak intensity of the P(1) and P(2) signals (including spinning side bands) for KVOPO_4 , as function of the refocalization delay.

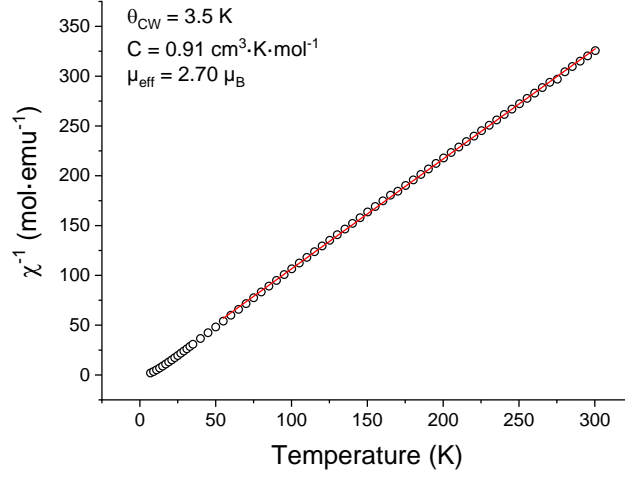


Figure S16: Inverse magnetic susceptibility of KVPO₄F measured in ZFC conditions with B=5000 Oe.

Table S7: Experimental cell parameters of KVPO₄F compared to those obtained from the structure optimized by the VASP code with different U_{eff} values.

	GGA	GGA+3eV	GGA+4eV	GGA+5eV	Experimental data
<i>a</i> (Å)	12.999	13.058	13.078	13.104	12.822
<i>b</i> (Å)	6.465	6.507	6.517	6.526	6.397
<i>c</i> (Å)	10.736	10.821	10.855	10.886	10.620
α	90°	90°	90°	90°	90°
β	90°	90°	90°	90°	90°
γ	90°	90°	90°	90°	90°

Table S8: Average V–O and V–F distances in KVPO₄F obtained from SXRD and structural optimization by the VASP code with different U_{eff} values.

	GGA	GGA+3eV	GGA+4eV	GGA+5eV	Experimental data
d _{V(1)–O} (Å)	1.98	2.02	2.03	2.03	1.98
d _{V(1)–F} (Å)	2.00	2.02	2.03	2.04	1.97
d _{V(2)–O} (Å)	2.01	2.04	2.04	2.05	1.99
d _{V(2)–F} (Å)	2.00	2.03	2.04	2.04	2.00

Table S9: Experimental cell parameters of KVOPO_4 compared to those obtained from the structure optimized by the VASP code with different U_{eff} values.

	GGA	GGA+3eV	GGA+4eV	GGA+5eV	Experimental data
a (Å)	12.870	12.968	12.991	12.997	12.762
b (Å)	6.439	6.468	6.471	6.478	6.365
c (Å)	10.522	10.586	10.588	10.593	10.513
α	90°	90°	90°	90°	90°
β	90°	90°	90°	90°	90°
γ	90°	90°	90°	90°	90°

Table S10: Average V–O distances in KVOPO_4 obtained from SXRD and structural optimization by the VASP code with different U_{eff} values.

	GGA	GGA+3eV	GGA+4eV	GGA+5eV	Experimental data
$d_{\text{V(1)-O}}$ (Å)	1.84	1.73	1.75	1.76	1.68
$5 \times d_{\text{V(1)-O}}$ (Å)*	1.98(6)	2.03(3)	2.03(3)	2.03(4)	1.99(1)
$1 \times d_{\text{V(2)-O}}$ (Å)	1.75	1.73	1.75	1.76	1.67
$1 \times d_{\text{V(2)-O}}$ (Å)	2.08	2.08	2.08	2.08	2.22
$4 \times d_{\text{V(2)-O}}$ (Å)*	1.97(11)	2.01(4)	2.01(3)	2.01(2)	2.04(4)

* Average values are given

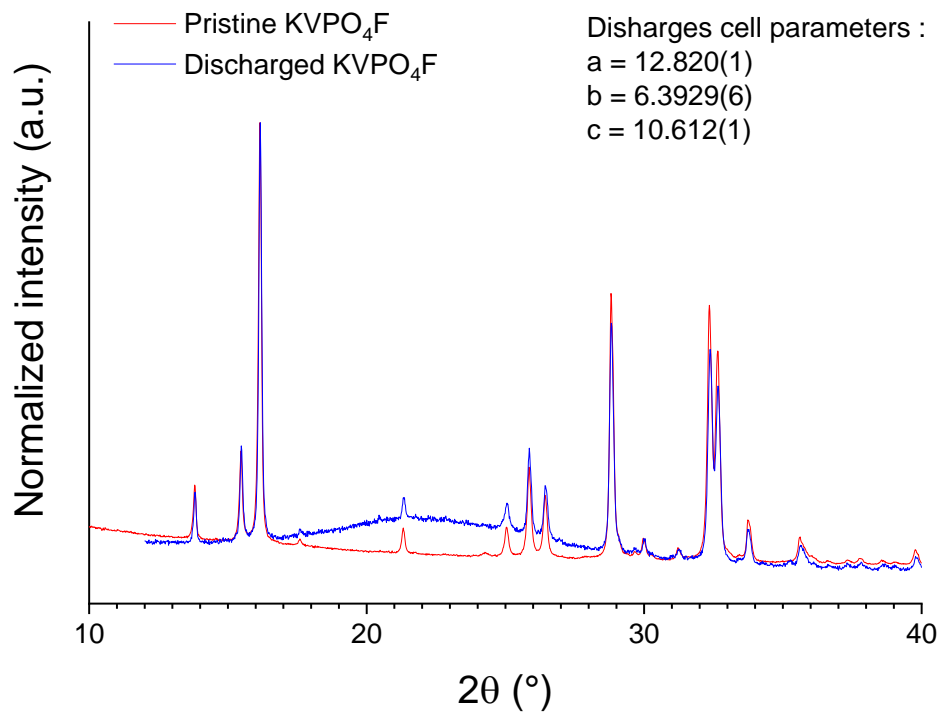


Figure S17: XRD patterns of pristine KVPO₄F and recovered electrode after 1 full cycle. Besides the large contribution between 15° and 30°, attributed to the glass capillary of the *ex situ* measurement, the peaks superpose which accounts for the reversibility of K⁺ (de)insertion.

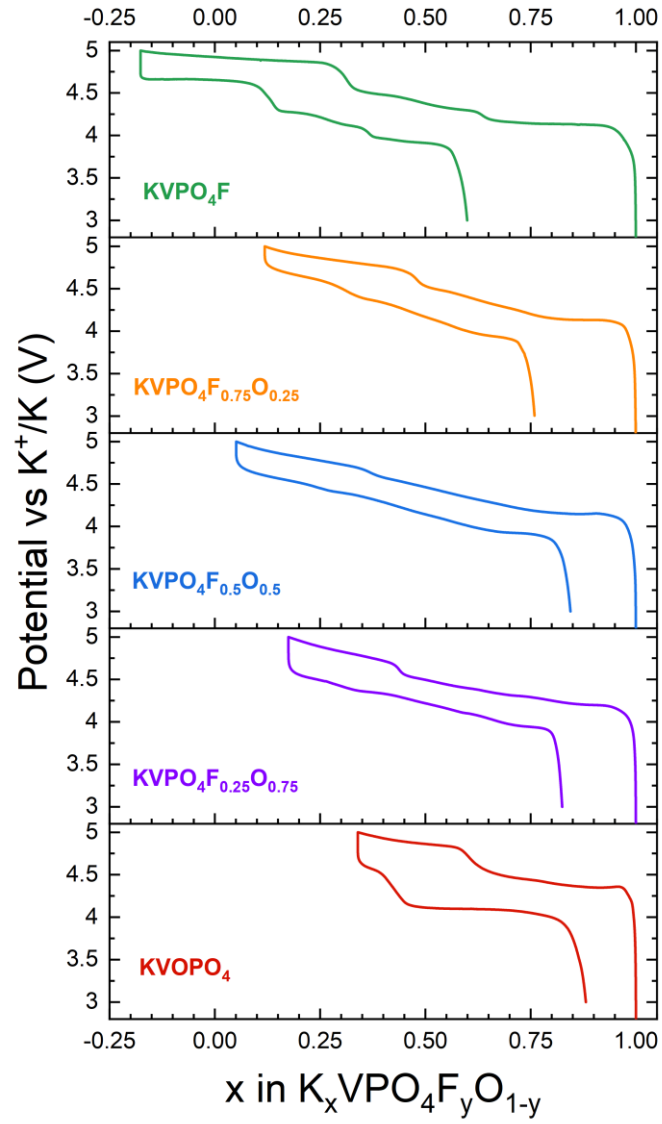


Figure S18: First cycle galvanostatic curves at C/20 in half cells.