SUPPORTING INFORMATION

Stabilization of a vanadium based hexagonal tungsten bronze hydroxyfluoride HTB-$(Fe_{0.55}V_{0.45})F_{2.67}(OH)_{0.33}$ as positive electrode for lithium-ions batteries

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Table S1. Data collection and structural parameters of $Fe_{1.64}V_{1.36}F_8(H_2O)_2$ with the *C*2/*m* space group obtained by powder diffraction.

Formulation	**$Fe_{1.64}V_{1.36}F_8(H_2O)_2$**	**Distances (Fe/V)-F/O (Å)**
System / Space Group	Monoclinic / *C*2/*m*	4x Fe(1)-O(1) = 2.14(1) 2x Fe(1)-F(3) = 2.04(1) 2x (Fe(2)/V(1))-F(1) = 1.91(1) 2x (Fe(2)/V(1))-F(2) = 1.94(1) 2x (Fe(2)/V(1))-F(3) = 1.89(1) ∑(Fe(1)) = 2.05 ∑(Fe(2)/V(1)) = 3.24
a (Å), b (Å), c (Å), β(°)	7.5835(3), 7.4814(3), 7.5269(3), 119.925(3)	
V (Å^3), Z	370.1(1), 2	
Wavelength (Å)	CuK_α	
$\rho_{calc.}$ (g cm^{-3})	3.122	
2θ (°)	5 – 150	
Unique refl.	406	
Refined param.	84	
R_p / R_{wp}	0.223 / 0.132	
R_B / R_f	0.040 / 0.057	
χ^2	2.05	

Table S2. Atomic coordinates and equivalent ADP of $Fe_{1.64}V_{1.36}F_8(H_2O)_2$.

Atom	**Site**	**x**	**y**	**z**	**occupancy**	**B_{eq} (Å^2)**
Fe^{2+}(1)	2b	0	½	0	1	3.3(1)
Fe^{3+}(2)	4f	¼	¼	½	0.32	1.7(1)
V^{3+}(1)	4f	¼	¼	½	0.68	1.7(1)
O(1)	4i	0.2088(10)	0	-0.0183(14)	1	3.9(1)
F(1)	4h	0	0.2142(10)	½	1	3.9(1)
F(2)	4i	0.2412 (11)	0	0.4253(10)	1	3.9(1)
F(3)	8j	0.1008(11)	0.3027(5)	0.2160(4)	1	3.9(1)

Table S4. Data collection and structural parameters of HTB-$(Fe_{0.55}V_{0.45})F_{2.67}(OH)_{0.33}$ with the *Cmcm* space group obtained by powder diffraction.

Formulation	**$(Fe_{0.55}V_{0.45})F_{2.67}(OH)_{0.33}$**	**Distances (Fe/V)-F/O (Å)**
System / Space Group	Orthorhombic / *Cmcm*	4x Fe(1)-F(2) = 1.90(1) 2x Fe(1)-F(3) = 1.92(1) 2x (Fe(2)/V(2))-F(2)/O(2) = 1.83(2) 2x (Fe(2)/V(2))-F(1) = 2.19(1) 2x (Fe(2)/V(2))-F(4) = 1.90(1)
a (Å), b (Å), c (Å)	7.296(1), 12.614 (1), 7.447(1)	
V (Å^3), Z	357.5(1), 6	
Wavelength (Å)	CoK_α	
$\rho_{calc.}$ (g cm^{-3})	3.081	
2θ (°)	5 – 150	
Unique refl.	283	
Refined param.	21	
R_p / R_{wp}	0.523 / 0.265	
R_B / R_f	0.088 / 0.121	
χ^2	1.87	

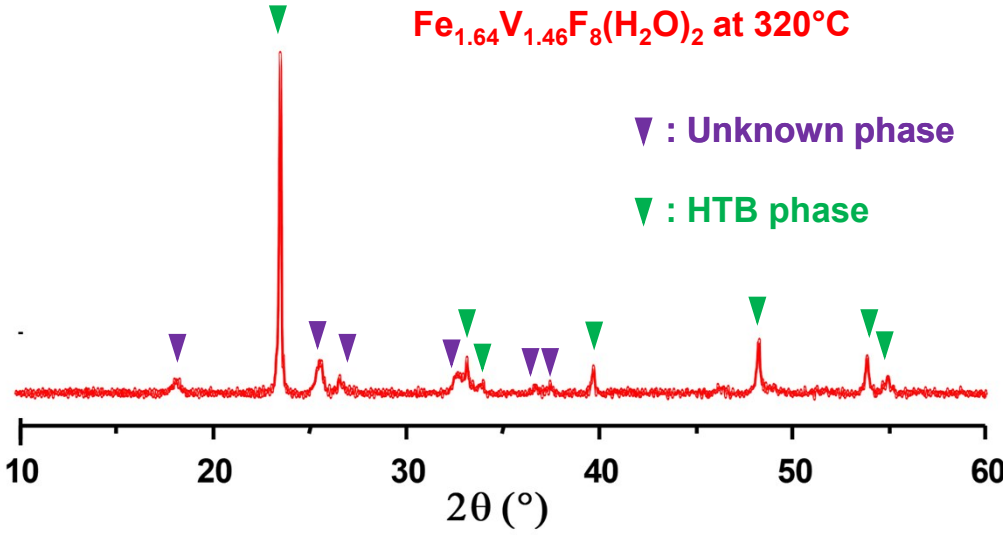

Figure S1. Diffraction pattern reccorded at 320°C during the *in situ* eperiment.

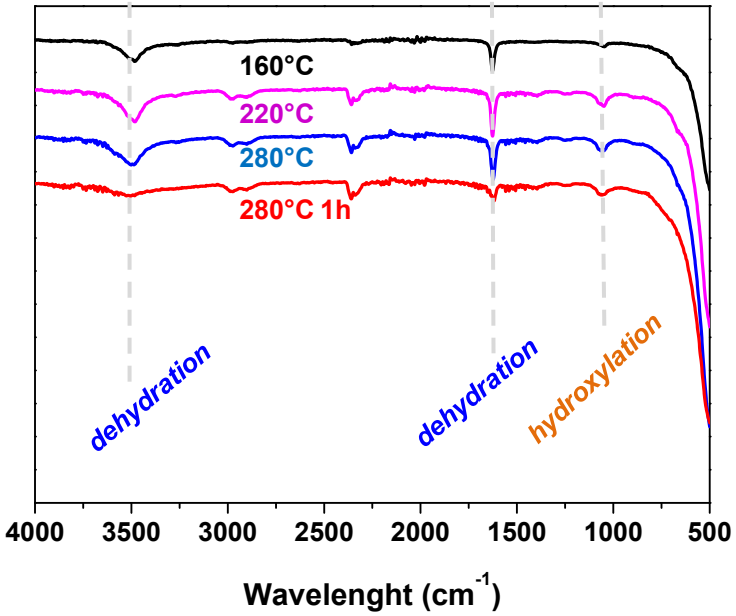

Figure S2. Evolution of the IR spectra of $Fe_{1.64}V_{1.36}F_8(H_2O)_2$ after treatment under air atmosphere at increasing temperatures.