Supplementary Information

Structural evolution of mixed valent (V^{3+}/V^{4+}) and V^{4+} sodium vanadium fluorophosphates as cathodes in sodium-ion batteries: Comparisons, overcharging and mid-term cycling

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Crystallographic parameters for overcharged V^{4+} material

Table S1. Crystallographic details of the overcharged $Na_{1.21(10)}V_2O_2(PO_4)_2F$ structure.

Atom	*x*	*y*	*z*	Site Occupancy Factor	Isotropic Atomic Displacement Parameter (× 100)/Å²
Na(1)	0.5091	0.252	0	0.60(6)	4.65
Na(2)	0.794	0.035	0	0.01(8)	8.05
V(1)	0.2411	0.2411	0.1807	1	3.48
P(1)	0	0.5	0.25	1	4.97
P(2)	0	0	0.2900	1	3.86
O(1)	0.099	0.412	0.1555	1	1.29
O(2)	0.101	0.101	0.153	1	1.29
O(3)	0.3750	0.3750	0.139	1	1.29
F(1)	0.270	0.270	0	1	1.41
"F(2)"	0.2256	0.2256	0.3288	1	7.54

Note only the Na site occupancy factors refined as the model was fairly stable (and this was tested)

χ^2 = 1.4, Rp = 2.06%, wRp = 2.77%, *a* = 8.83551(23), *c* = 10.8901(10) Å

Crystallographic parameters for overcharged Mixed valent sample

Table S2. Crystallographic details of the overcharged $Na_{0.508}V_2O_{1.6}(PO_4)_2F_{1.4}$ structure.

Atom	*x*	*y*	*z*	Site Occupancy Factor
Na(1)	0.5495	0.2155	0	0
Na(2)	0.7403	-0.0353	0	0.254(12)
V(1)	0.2441	0.2441	0.1877	1
P(1)	0	0.5	0.25	1
P(2)	0	0	0.23	1
O(1)	0.0854	0.3954	0.1444	1
O(2)	0.0994	0.0994	0.1576	1
O(3)	0.3916	0.3916	0.1558	1
F(1)	0.2855	0.2855	0	1
"F(2)"	0.2890	0.2890	0.3509	1

Note only the Na site occupancy factors refined following the stepwise refinement of other parameters.

χ^2 = 1.32, Rp = 1.88%, wRp = 2.53%, *a* = 8.86077(23), *c* = 10.9307(5) Å