

Supporting information

Na-ion storage in iron hydroxide phosphate hydrate through a reversible crystalline-to-amorphous phase transition

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Table S1. Results of the Rietveld refinement of the as-synthesized $\text{Fe}_{1.13}(\text{PO}_4)(\text{OH})_{0.39}(\text{H}_2\text{O})_{0.61}$ (Figure 1).

Unit cell parameters [Å]		<i>a</i>	5.1702(3)	<i>c</i>	13.0600(14)
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}	Occupancy
Fe1	0	1/2	0	0.93	0.56(2)
P1	1/2	1/4	1/8	0.70	1.00
O1	0	3/4	1/8	= <i>B</i> _{iso} (P)	1.00
O2	0.25574	1/4	0.06010	= <i>B</i> _{iso} (P)	1.00
H1	0	3/4	1/8	= <i>B</i> _{iso} (P)	1.00
Agreement factors		<i>R</i> _{Bragg} = 6.61%	<i>R</i> _p = 12.1%	<i>R</i> _{wp} = 23.7%	$\chi^2 = 0.817 \cdot 10^6$

Table S2. Results of refinement for the PDF of the as-synthesized FPOH material.

Parameter	Crystalline FPOH
Scale Factor	0.282 ± 0.017
<i>a</i> [Å]	5.1797 ± 0.0027
<i>c</i> [Å]	13.079 ± 0.012
δ_2 [Å ²]	2.21 ± 0.14
<i>spd</i> [Å]	144 ± 30
<i>u</i> _{11,Fe} [Å ²]	0.0052 ± 0.0042
<i>u</i> _{22,Fe} [Å ²]	0.0384 ± 0.0093
<i>u</i> _{33,Fe} [Å ²]	0.0085 ± 0.0037
<i>u</i> _{13/23,Fe} [Å ²]	0.0092 ± 0.0056
<i>u</i> _{11,22P} [Å ²]	0.0096 ± 0.0037
<i>u</i> _{33,P} [Å ²]	0.0094 ± 0.0057
<i>u</i> _{11/22,O1} [Å ²]	0.065 ± 0.027
<i>u</i> _{33,O1} [Å ²]	0.031 ± 0.032
<i>u</i> _{11,O2} [Å ²]	0.053 ± 0.021
<i>u</i> _{22,O2} [Å ²]	0.024 ± 0.012
<i>u</i> _{33,O2} [Å ²]	0.061 ± 0.021
<i>u</i> _{13/23,O2} [Å ²]	-0.031 ± 0.018
<i>x</i> _{O2} [<i>a</i>]	0.2488 ± 0.0042
<i>z</i> _{O2} [<i>c</i>]	0.0606 ± 0.0021
<i>r</i> _w	0.21

Table S3. Results of refinement of the PDF for the discharged material, Na_{0.83}FPOH.

Parameter	Ordered Na _x FPOH	Amorphous Na _x FPOH	Graphite
Scale Factor	0.090 ± 0.023	0.49 ± 0.25	0.030 ± 0.023
<i>a</i> [Å]	5.268 ± 0.021	5.6 ± 0.1	2.470 ± 0.017
<i>c</i> [Å]	13.1 ± 0.1	10.82 ± 0.41	-
δ ₂ [Å ²]	3.43 ± 0.95	1.94 ± 0.37	2.9 ± 8.1
<i>spd</i> [Å]	53 ± 18	5.8 ± 1.1	16 ± 12
<i>u</i> _{iso,Fe} [Å ²]	0.0149 ± 0.0089		-
<i>u</i> _{iso,P} [Å ²]	0.0235 ± 0.021		-
<i>u</i> _{iso,O1} [Å ²]	1.3 ± 1.1		-
<i>u</i> _{iso,O2} [Å ²]	0.029 ± 0.022		-
<i>u</i> _{iso,C} [Å ²]	-		0.0021 ± 0.0031
<i>r</i> _w	0.33		

Table S4. Results of refinement of the PDF for the recharged material, Na_{0.02}FPOH. The asterisk of the coherent domain size of the graphite phase indicates that it was fixed.

Parameter	Ordered FPOH	Disordered FPOH	Graphite
Scale Factor	0.171 ± 0.019	0.26 ± 0.15	0.030 ± 0.015
<i>a</i> [Å]	5.2060 ± 0.0045	5.4 ± 0.2	2.472 ± 0.014
<i>c</i> [Å]	13.055 ± 0.025	10.89 ± 0.71	-
δ ₂ [Å ²]	2.1 ± 0.3	1.85 ± 0.64	3.9 ± 5.3
<i>spd</i> [Å]	120 ± 36	6.8 ± 2.2	18*
<i>u</i> _{iso,Fe} [Å ²]	0.0119 ± 0.0031		-
<i>u</i> _{iso,P} [Å ²]	0.0143 ± 0.0057		-
<i>u</i> _{iso,O1} [Å ²]	0.039 ± 0.016		-
<i>u</i> _{iso,O2} [Å ²]	0.042 ± 0.012		-
<i>u</i> _{iso,C} [Å ²]	-		0.0021 ± 0.0024
<i>r</i> _w	0.26		

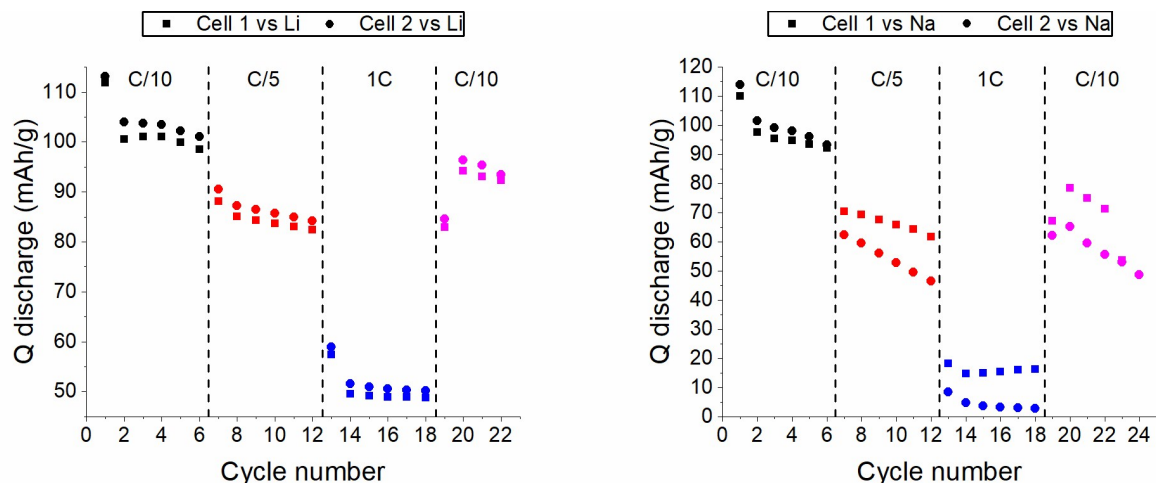


Figure S1. Rate capability tests of FPOH against (left) Li anode and (right) Na anode. Two cells were measured against each anode and the consecutive current rates were performed on the same cell, but with relaxation between current rates.

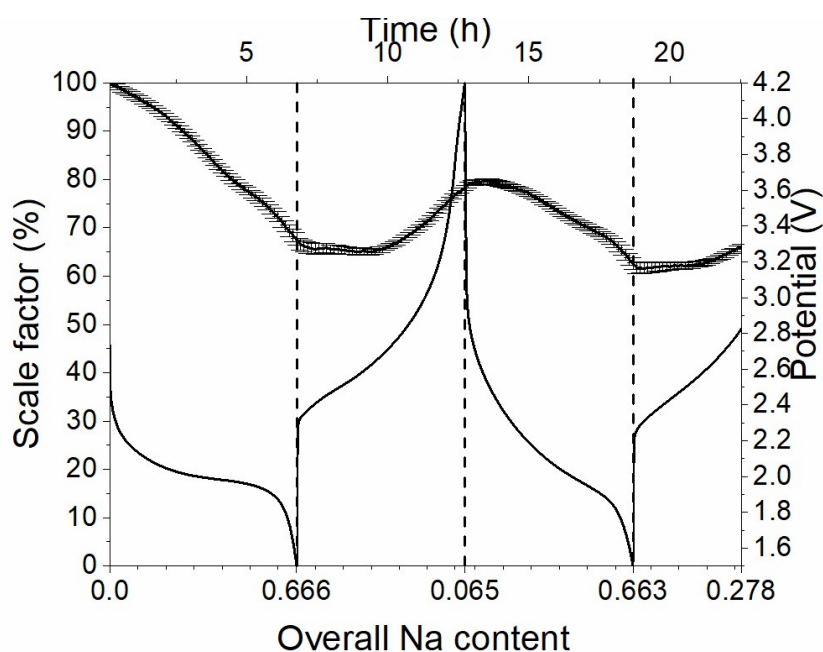


Figure S2. Scale factor (extracted from Rietveld refinement of the *operando* PXRD data) for the crystalline Na_xFPOH phase as a function of Na-content in the electrode.

