

Supporting Information

Impact of synthesis conditions in Na-rich Prussian Blue Analogs

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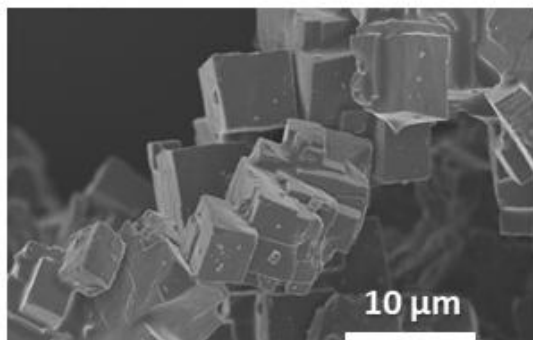
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(a) Na-FeHCF-reflux-107°C



(b) Na-FeHCF-Vac-220°C

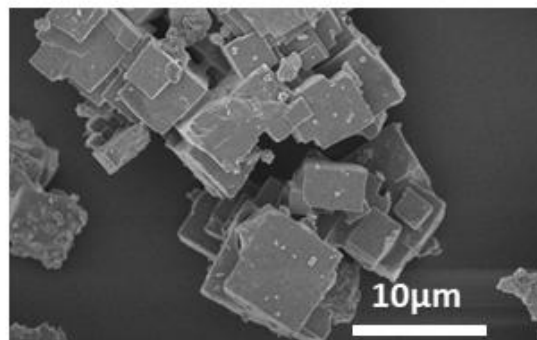


Figure S1: SEM images of (a) Na-FeHCF-reflux-107°C and (b) Na-FeHCF-Vac-220°. Scale bar is 10 μm.

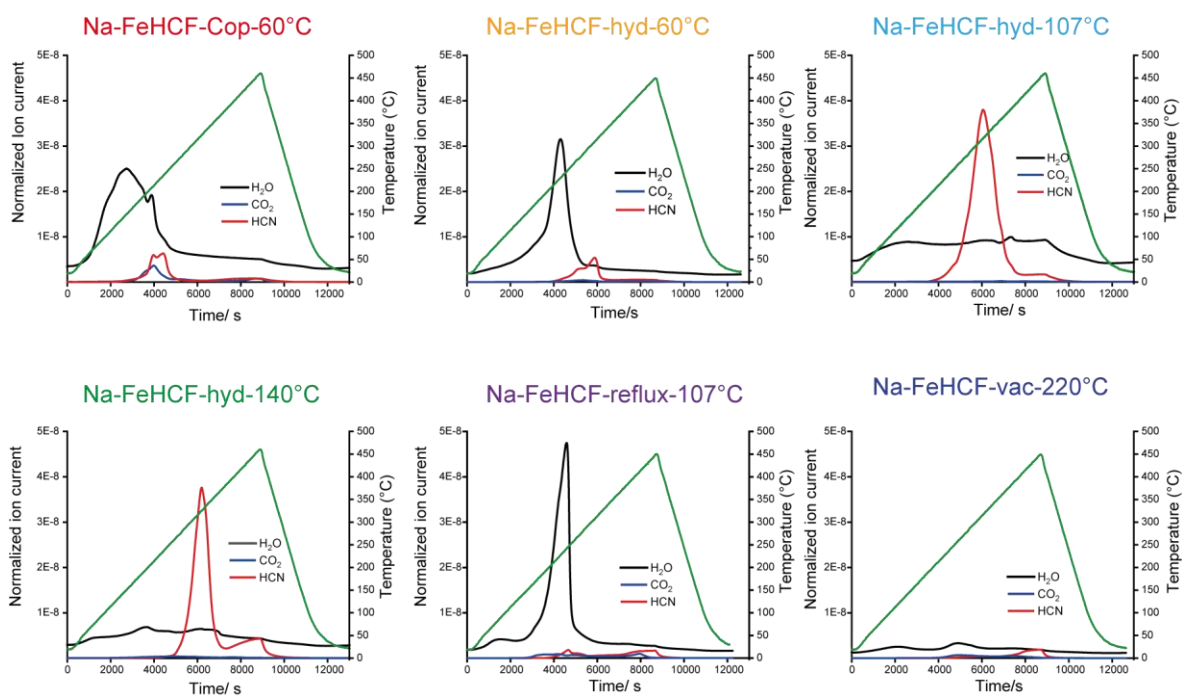


Figure S2: TGA-Ms spectra for (a) Na-FeHCF-Cop-60°C, (b) Na-FeHCF-hyd-60°C, (c) Na-FeHCF-hyd-107°C, (d) Na-FeHCF-hyd-140°C, (e) Na-FeHCF-reflux-107°C and (f) Na-FeHCF-Vac-220°C.

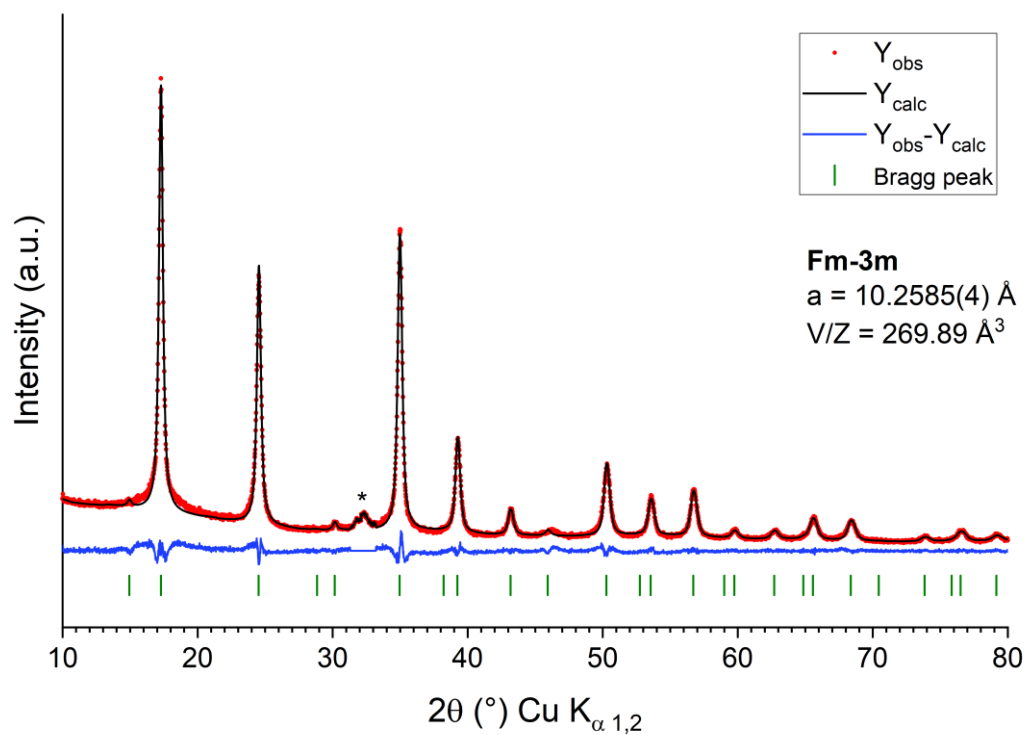


Figure S3: Result of the full pattern matching performed in the **Fm-3m** space group of the X-ray powder diffraction data recorded for Na-FeHCF-Cop-60°C. A small unidentified impurity is marked by *.

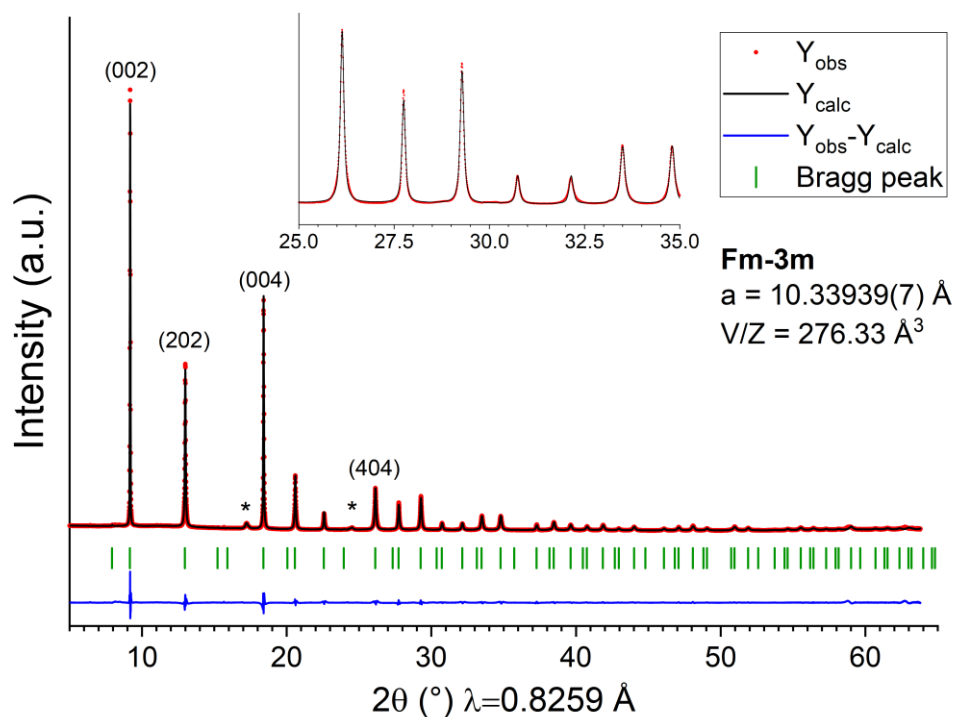


Figure S4: Result of the Rietveld refinement performed in the **Fm-3m** space group of the synchrotron X-ray powder diffraction pattern recorded for Na-FeHCF-hyd-60°C. Anisotropic particle size broadening model was used along the [101] direction to account for the broader line shapes observed for (202) and (404) peaks. An unidentified impurity is marked by *.

Table S5: Atomic coordinates determined by the Rietveld refinement performed in the **Fm-3m** space group of the X-ray powder diffraction data recorded for Na-FeHCF-hyd-60°C.

Na_{1.36}Fe₂(CN)₆·1.86H₂O						
<i>S.G. Fm-3m</i>		$a = b = c = 10.33939(7) \text{ \AA}$			$R_{\text{Bragg}} = 2.28$	
$Z = 4$		$V/Z = 276.33 \text{ \AA}^3$			$R_p = 5.93$	
					$R_{\text{wp}} = 7.80$	
Atoms	Wyckoff positions	x/a	y/b	z/c	Occupancy	B_{iso}
Fe (1)	4a	0	0	0	1	0.5
Fe (2)	4b	½	½	½	1	0.5
Na	8c	¼	¼	¼	0.68(3)	2.21(8)
C	24e	0.1765(4)	0	0	1	0.7
N	24e	0.2886(4)	0	0	1	0.7
O	24d	¼	¼	0	0.31(1)	1

Bond	Distance (Å)
Fe (1) - C	1.876(5)
Fe (2) - N	2.091(1)
C - N	1.201(3)
Na - O	2.584(6)

Table S6: Proposed chemical composition for each Na-FeHCF material depending on the results of each technique used.

Na-FeHCF	Proposed Compositions			
	TGA	PXRD	Mössbauer (Fe)*	Electrochemical (Na) insertion tests
Na-FeHCF-Cop-60°C	1.6 H ₂ O	-	Fe _{LS} ^{II} _{0.41} Fe ^{III} _{0.57} Fe _{HS} ^{II} _{0.02}	Na _{1.4} Fe ₂ (CN) ₆
Na-FeHCF-hyd-60°C	1.36 H ₂ O	Na_{1.36}Fe₂(CN)₆·1.86 H₂O	Fe _{LS} ^{II} _{0.38} Fe ^{III} _{0.27} Fe _{HS} ^{II} _{0.35}	Na _{1.4} Fe ₂ (CN) ₆
Na-FeHCF-hyd-107°C	0.6 H ₂ O	-	Fe _{LS} ^{II} _{0.49} Fe ^{III} _{0.05} Fe _{HS} ^{II} _{0.46}	-
Na-FeHCF-hyd-140°C	0.7 H ₂ O	-	Fe _{LS} ^{II} _{0.5} Fe _{HS} ^{II} _{0.5}	Na _{1.8} Fe ₂ (CN) ₆
Na-FeHCF-reflux-107°C	2 H ₂ O	Na_{1.86}Fe₂(CN)₆·1.92 H₂O	Fe _{LS} ^{II} _{0.5} Fe _{HS} ^{II} _{0.5}	Na _{1.9} Fe ₂ (CN) ₆
Na-FeHCF-Vac-220°C	0.18 H ₂ O	-	Fe _{LS} ^{II} _{0.49} Fe ^{III} _{0.07} Fe _{HS} ^{II} _{0.44}	Na _{1.96} Fe ₂ (CN) ₆

[*]: The iron content is expressed as a percentage of the total signal.

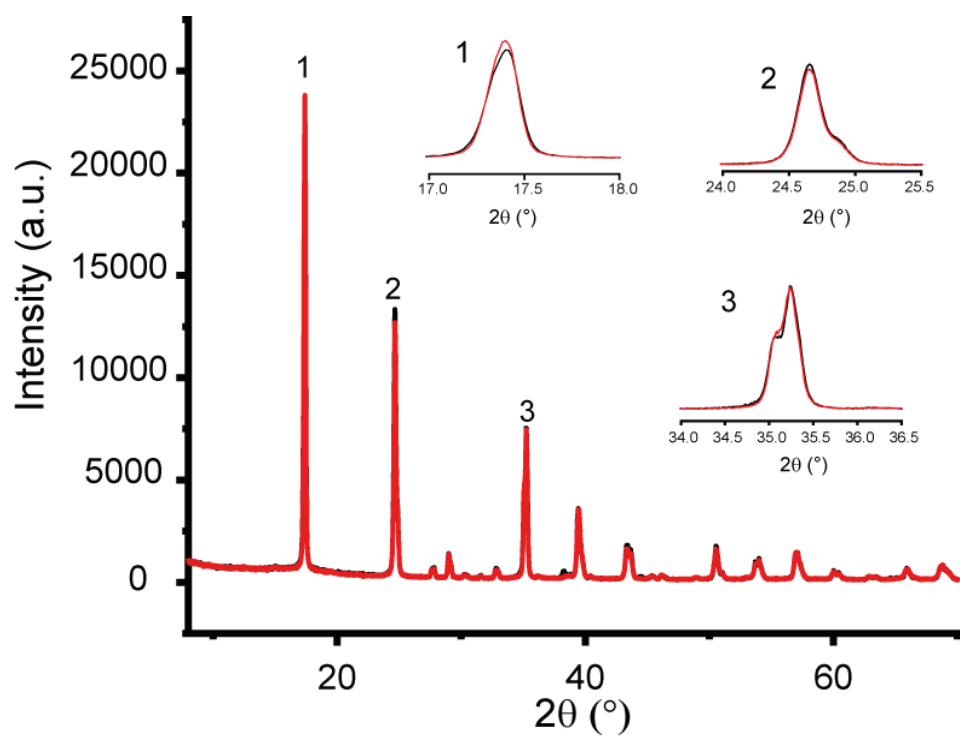


Figure S7: Laboratory X-ray powder diffraction data recorded for Na-FeHCF-hyd-107°C (red) and Na-FeHCF-hyd-140°C (black). Insets show the three more intense peaks in detail. The enlargement of peak 1 especially highlights the orthorhombic distortion observed in both patterns and corresponding to the (200) and (011) indexations.

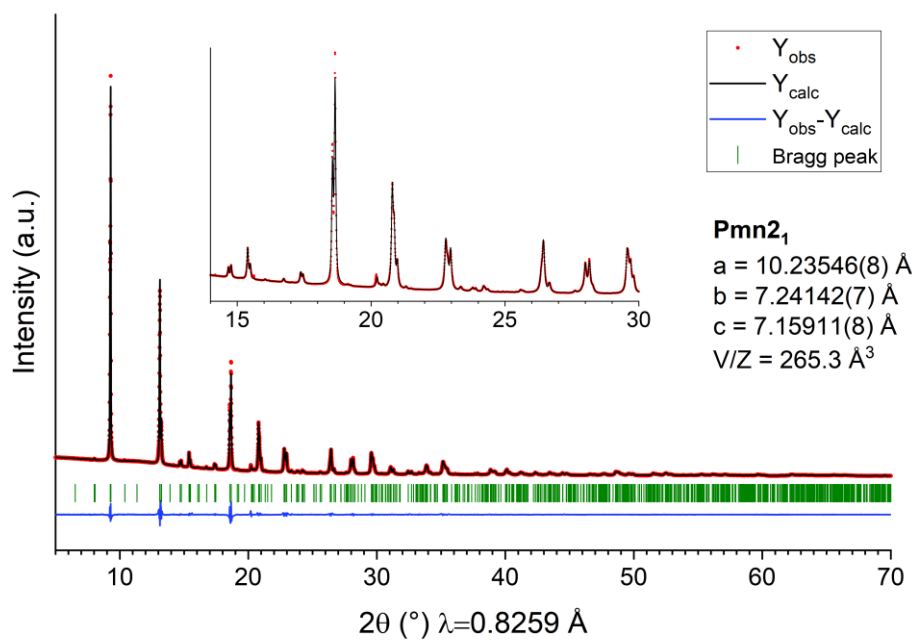
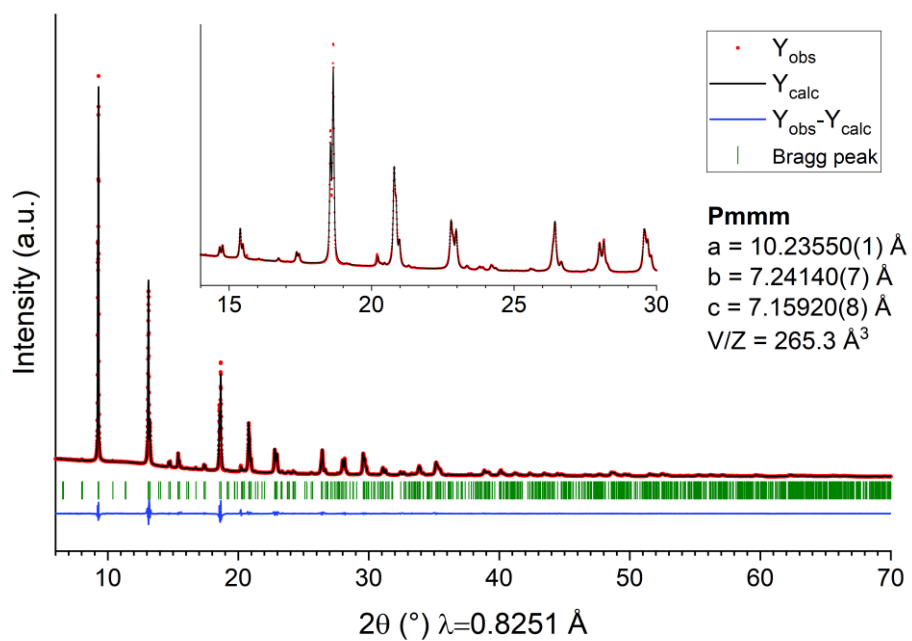


Figure S8: Results of the full pattern matching refinements performed in the orthorhombic **Pmmm** (top) and **Pmn2₁** (bottom) space groups of the X-ray powder diffraction data recorded for Na-FeHCF-hyd-140°C.

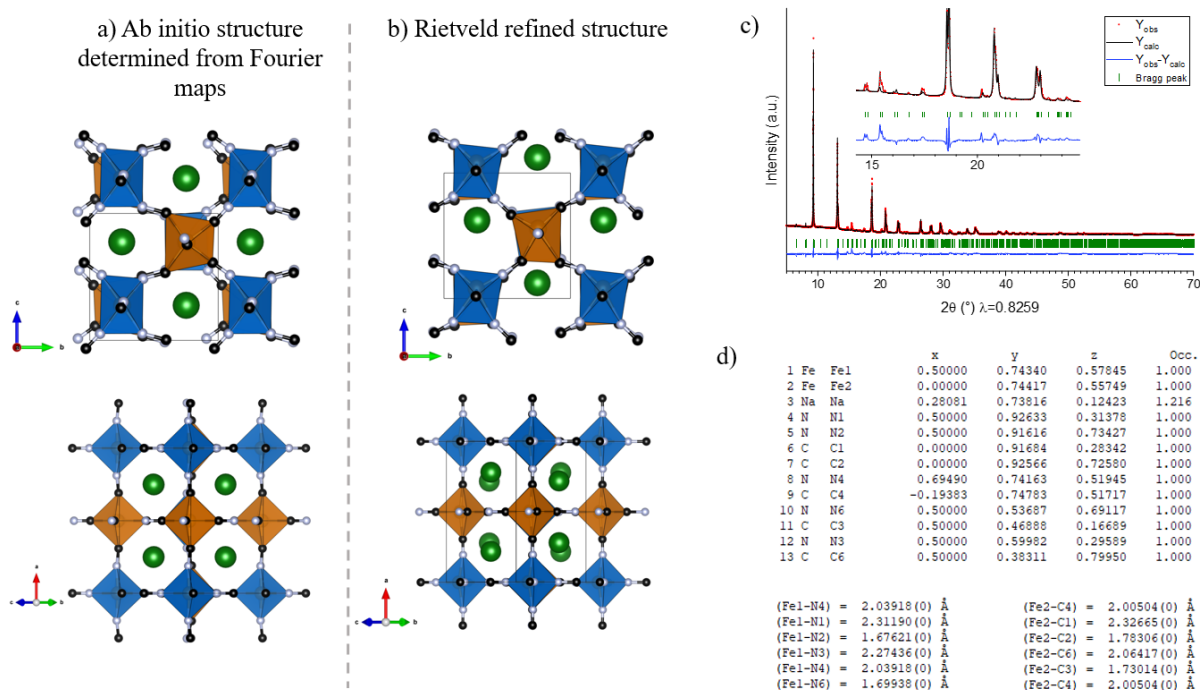


Figure S9: a) Results from the ab initio structure determination attempt for Na-FeHCF-hyd-140°C with the structure determined with Fourier difference maps performed after positioning heavy Fe and Na with SUPERFLIP (included in JANA2006) in the $Pmn2_1$ spacegroup. b) Structure after refinement of atomic positions. c) Corresponding experimental data-fit agreement. Despite the very good fit in full pattern matching refinement, and the possibility to construct the PBA framework in $Pmn2_1$ space group, the refined structure has not been retained due to the very distorted sites that are unlikely and the bad fitting of low intensity peaks. d) The corresponding atomic coordinates and occupancies are given in the table, along with the Fe-C/N distances.

We suggest that this disagreement is either due to the use of an incorrect space group or to crystalline preferred orientation which hinders the intensity matching between experimental and refined XRD pattern. Attempts to determine the structure on a crystal selected in the powder Na-FeHCF-hyd-140°C were performed, without any success due to the small size of the crystals.

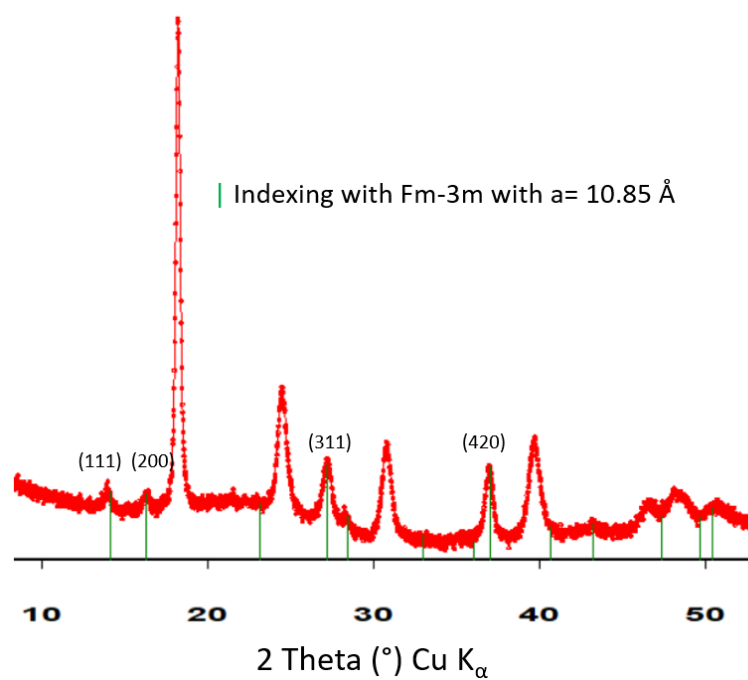


Figure S10: Unsuccessful attempt to index the diffraction pattern of Na-FeHCF-Vac-220°C with a cubic symmetry (Fm-3m). The intense peak at $2\theta = 18.25^\circ$ is characteristic of the $(012)_{R-3}$ reflection plane.

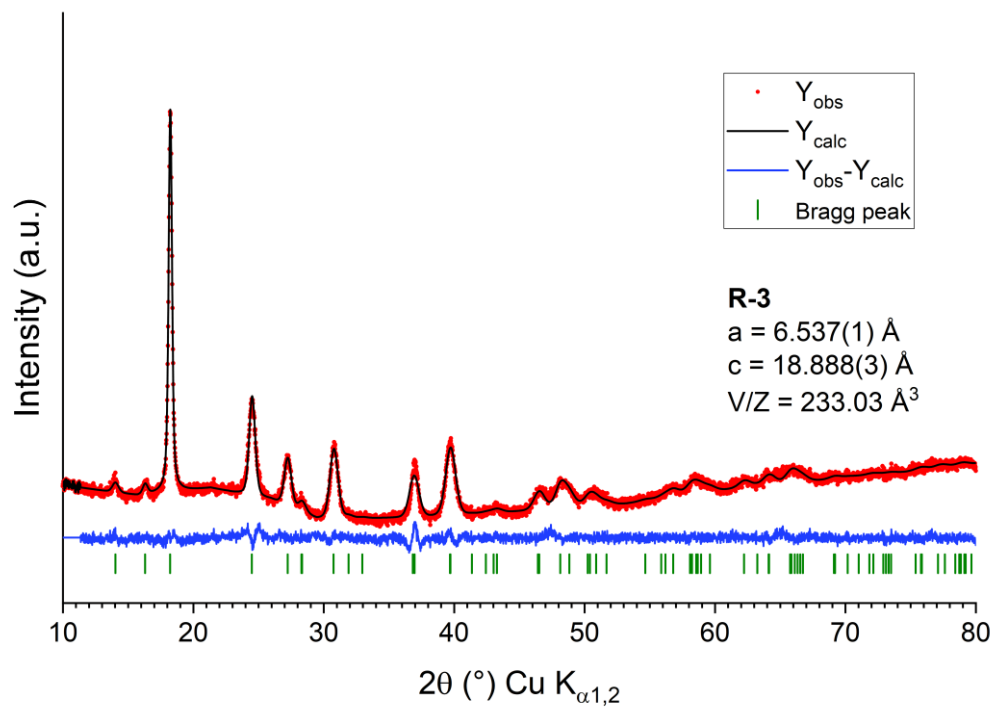


Figure S11: Result of the full pattern matching performed in the **R-3** space group of the X-ray powder diffraction data recorded for Na-FeHCF-Vac-220°C.

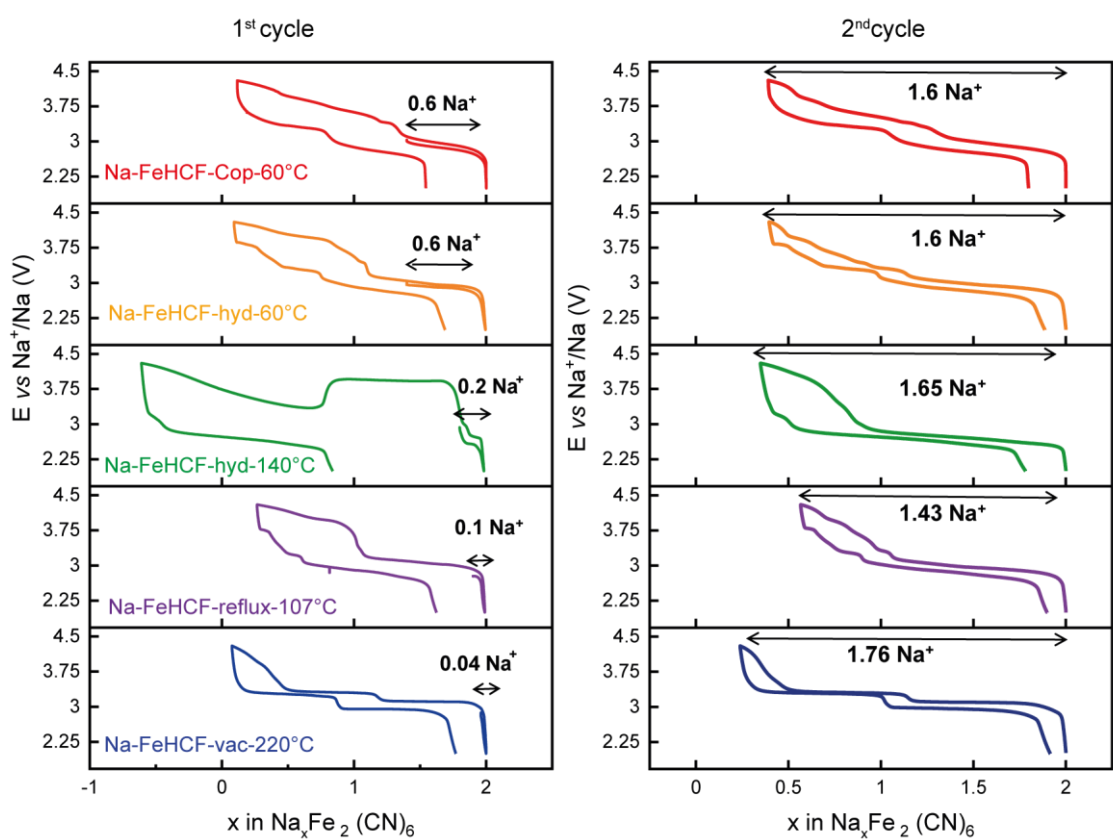


Figure S12: Electrochemical curves obtained starting the Na half-cells in discharge, with Na-FeHCFs at the positive electrode: cycling rate of $C/20$ per Na^+ , with the cut-off voltage of 4.3 V vs. Na^+/Na .

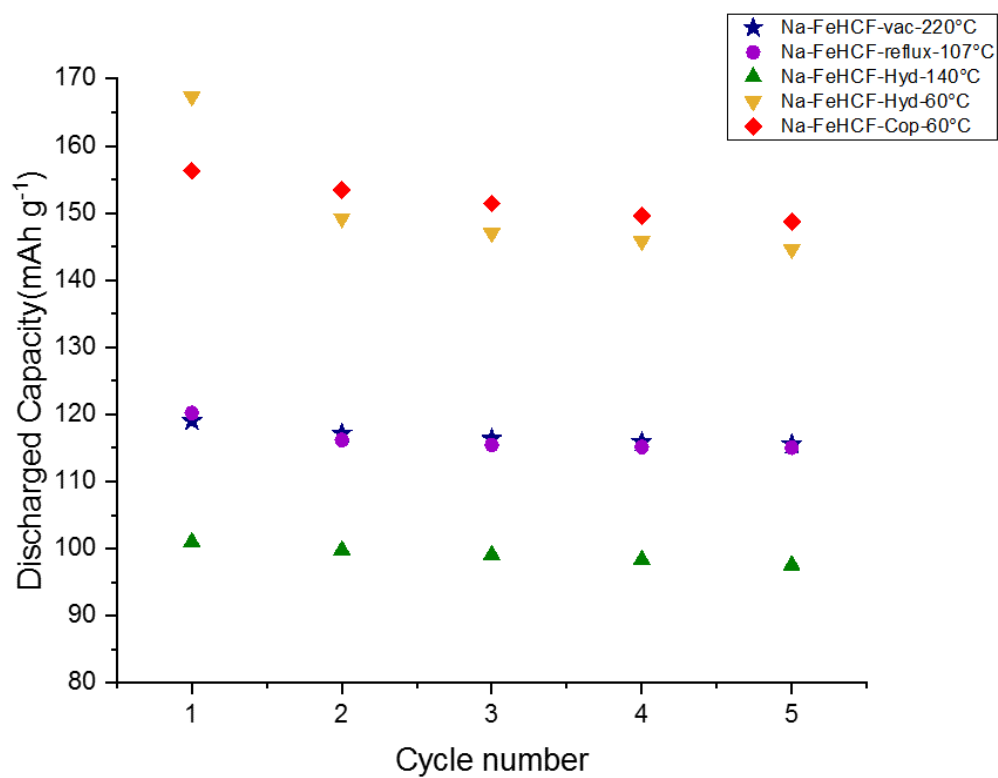


Figure S13: Discharge capacity determined for Na-FeHCFs materials in Na half-cells during the first 5 cycles, at a cycling rate of C/20 per Na⁺ and with the cut-off voltage of 4.3 V vs. Na⁺/Na.