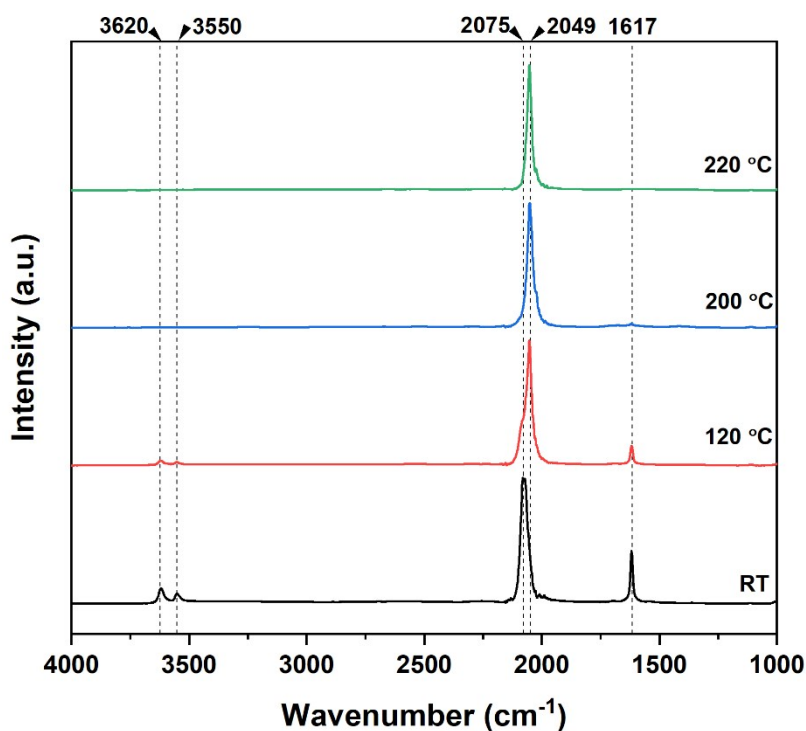


Supplementary Information for

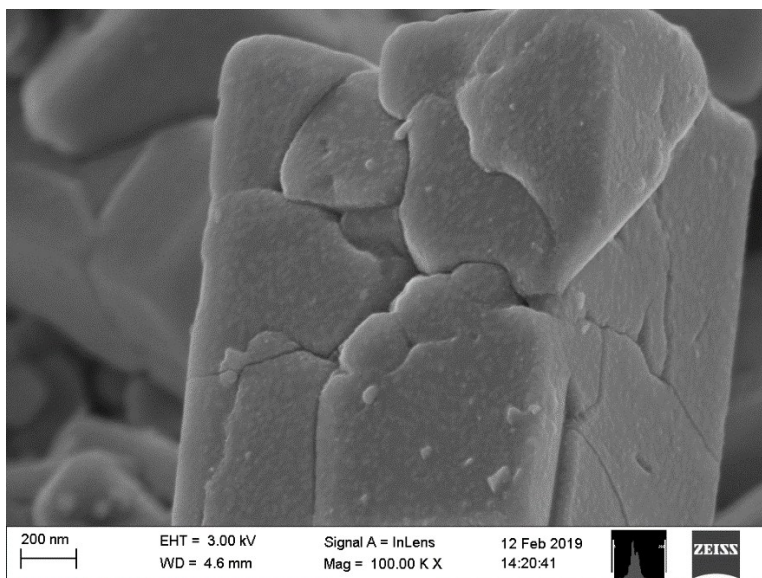
## Influence of sodium content on the thermal behavior of low vacancy Prussian white cathode material

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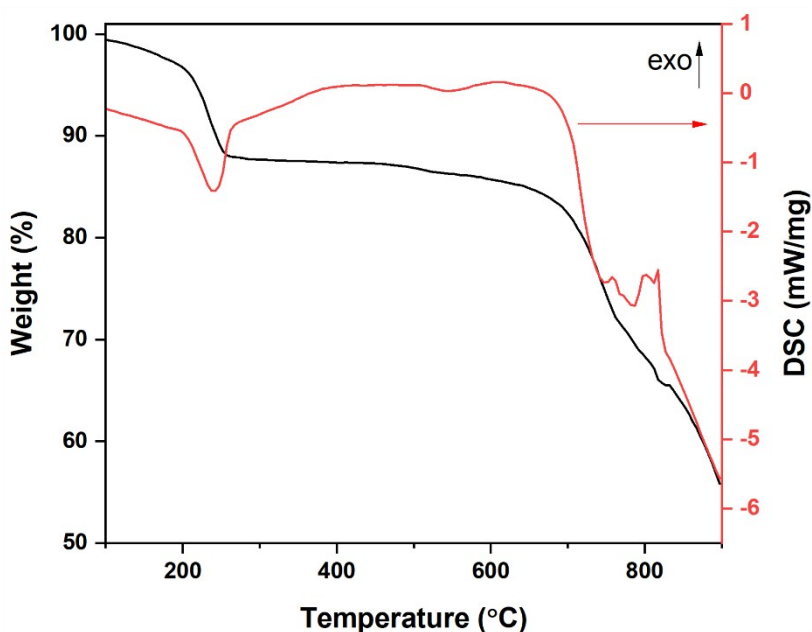
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**Figure S1.** IR spectra of Na<sub>1.5</sub> annealed at 120 °C, 200 °C and 220 °C under vacuum for 24 h. When heated to 120 °C the intensities of the O-H stretching absorption bands in the region 3620-3550 cm<sup>-1</sup>, and the O-H-O bending mode at 1617 cm<sup>-1</sup> are observed to decrease. Upon heating to 200 °C, the O-H bands have vanished completely, while the O-H-O band appears very weak and broad. No water band is observed at 220 °C, implying complete dehydration.



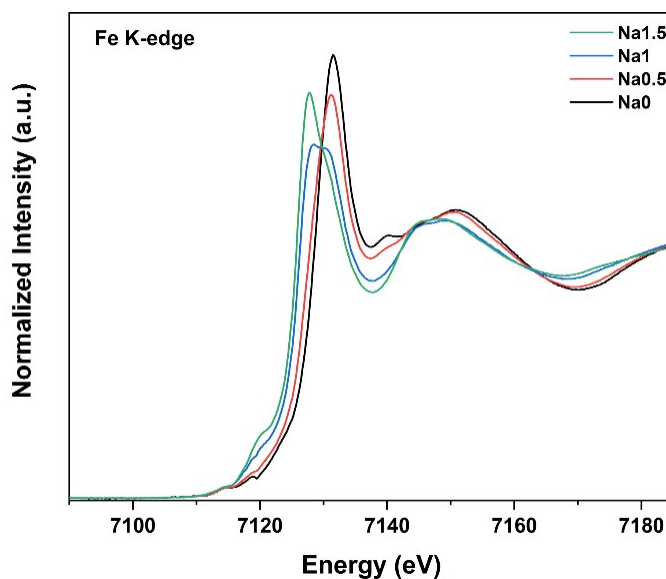
**Figure S2.** SEM image showing particle cracks during water release.



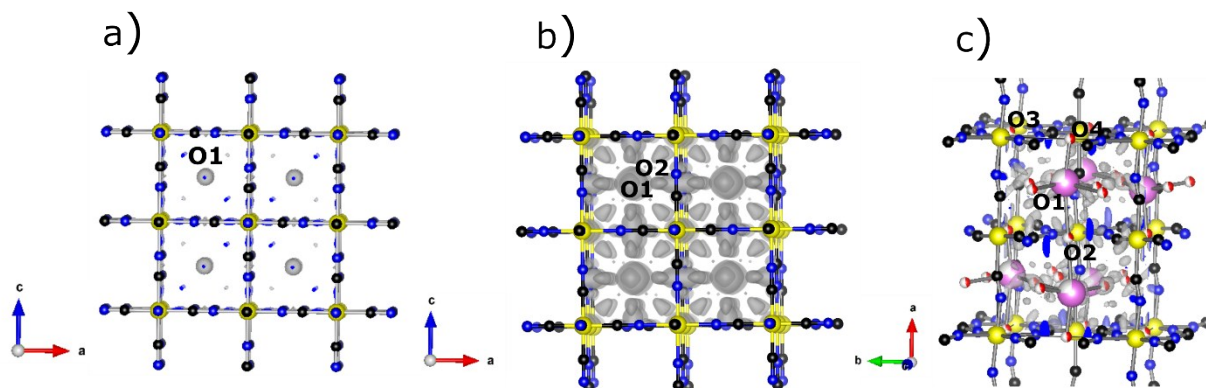
**Figure S3.** TG-DSC curves for Na<sub>1.5</sub> recorded in Ar at a heating rate of 5 °C/min.

X-ray absorption near edge structure (XANES) measurements were performed at the Fe K-edge to determine the formal charges of the Fe cations in Na<sub>1.5</sub>, Na<sub>1</sub>, Na<sub>0.5</sub> and Na<sub>0</sub> samples. The samples were mixed with BN (20:80 w/w) and pressed into 1 mm thick pellets. The measurements were performed at room temperature at the Balder beamline at MAX IV synchrotron radiation source at Lund, Sweden. Spectra at the K-edge for Fe were acquired in transmission mode. The spectrum of an iron foil was recorded simultaneously during collection of the transmission data and used for energy calibration. All data treatment were performed using BESSY software.<sup>1</sup>

The edge position can be correlated to the formal charge state of the absorbing atom. A small shift in the Fe K-edge position towards lower energy from Na0 to Na1.5 is apparent (Fig. S4). The observed shift in the position of the absorption edge can be quantitatively related to the valence state of the Fe atom.

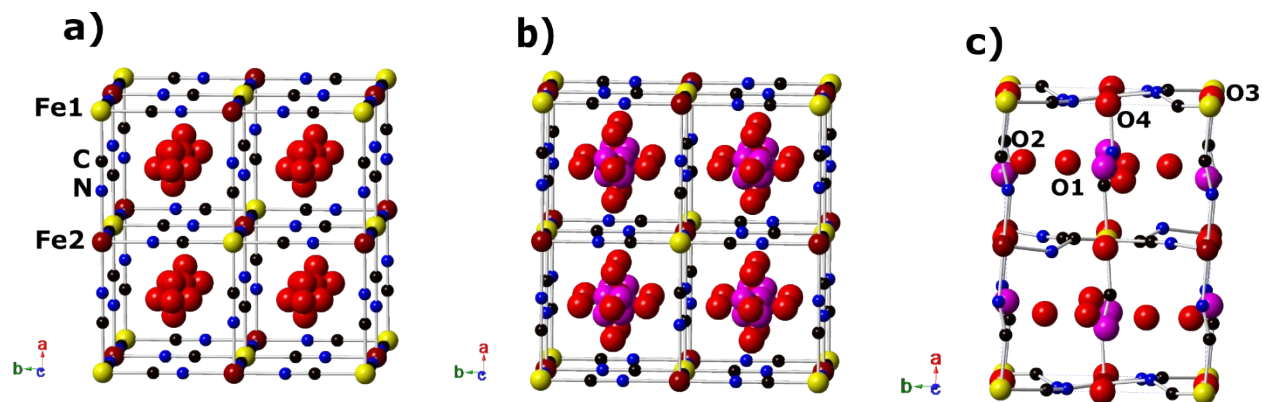


**Figure S4.** Normalized XANES spectra of Na1.5, Na1, Na0.5 and Na0 samples taken at the Fe K-edge.



**Figure S5.** Difference Fourier maps of a) Na0, b) Na1 and c) Na1.5 that include only the framework atoms (Fe, C and N) in the model, show significant peaks in the maps attributed to positions of the water molecules as marked. Fourier difference calculations were converted into 3D visualization maps using VESTA.<sup>2</sup> The approach employed to locate the Na and O positions from Fourier maps was to first fit a model containing only Fe, C and N atoms on positions defined in the literature;  $Fm\bar{3}m$  model for Na0, Na0.5 and Na1, while  $P2_1/n$  model was used for Na1.5. During the initial refinement cycles, only the background terms, peak shape profile terms, scale factors and lattice parameters were allowed to vary. No residual scattering intensities were seen at the positions of the framework atoms. However, there are two distinct peaks in the cavities, which can be assigned to water molecules. The O atoms were added to the model and their occupation parameter refined, while those for Na were fixed to ICP values. Attempts to refine Na and O occupation factors simultaneously yielded more Na atoms per formula unit compared to the ICP values. This is due to the similarities between the X-ray scattering factors of Na and O atoms. Collective refinement of the occupation factors and the  $B_{iso}$  for O atoms proved difficult. Such that high  $B_{iso}$  values,  $\sim 10 \text{ \AA}^2$  were observed, suggesting a smudgy position of the O sites in the cavity. Hence, different atoms were set to have

fixed  $B_{\text{iso}}$  values for which the refinements were stable. Moreover, soft constraints were used to limit the C-N distances to  $\sim 1.16$  Å.<sup>3,4,5,6</sup> Good fits could be achieved without the use of soft constraints on C-N distances, however, values for some interatomic bond distances and angles were doubtful. A summary of the refined lattice parameters, atomic positions, site occupancy factors (sofs), atomic displacement parameters ( $B_{\text{iso}}$ ) and derived chemical formula are presented in Tables S1-S4.



**Figure S6.** Crystal structures of a) Na0, b) Na1 and c) Na1.5 with all the atoms shown. The O atoms are shown in red and Na atoms in magenta. For Na0, the O atoms partially occupy site 48g forming an octahedron. For Na1, the O atoms are located at the center of the framework cavity (site 8c) and the site 48g, while the Na atoms partially occupy site 32f forming a tetrahedron. For Na1.5, four different O sites are clearly marked. The atomic coordinates for all atoms are given in the tables below.

**Table S1. Crystal structure data for (Na1.5)  $\text{Na}_{1.5}\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2.5(1)\text{H}_2\text{O}$ , space group  $P2_1/n$ ,  $a = 10.434(1)$  Å,  $b = 7.402(1)$  Å, and  $c = 7.311(1)$  Å;  $\beta = 92.09(1)^\circ$**

atom	sites	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )	sof	atoms per unit cell
Fe1	2a	0.5	0.5	0.5	0.8	1	2
Fe2	2d	0.5	0	0	0.8	1	2
C1	4e	0.508(8)	0.83(1)	0.164(9)	0.8	1	4
C2	4e	0.701(9)	0.99(1)	0.01(1)	0.8	1	4
C3	4e	0.486(7)	0.780(8)	0.77(1)	0.8	1	4
N1	4e	0.495(6)	0.755(9)	0.301(7)	0.8	1	4
N2	4e	0.189(7)	0.986(9)	-0.004(8)	0.8	1	4
N3	4e	0.494(7)	0.659(8)	0.673(7)	0.8	1	4
Na1	4e	0.777(3)	0.535(4)	0	4	0.75	3
O1	4e	0.75(1)	0.73(1)	0.27(1)	0.6	0.45(3)	1.8
O2	4e	0.249(8)	0.67(1)	0.18(1)	0.6	0.41(3)	1.6
O3	2b	0	0	0.5	0.6	0.31(5)	0.6
O4	2c	0	0.5	0	0.6	0.46(5)	0.9

$R_{\text{wp}} = 2.6\%$ ,  $R_{\text{exp}} = 3.8\%$ ,  $\chi^2 = 0.5^*$ ,  $R_B = 1.4$

atom	sites	x	y	z	$B_{iso}$ (Å <sup>2</sup> )	sof	atoms per unit cell
Fe1	4a	0	0	0	1.4	1	4
Fe2	4b	0.5	0	0	1.4	1	4
N1	24e	0.296(1)	0	0	1.4	1	24
C1	24e	0.180(1)	0	0	1.4	1	24
O1	8c	0.25	0.25	0.25	3	0.32(1)	2.6
O2	48g	0.470(2)	0.25	0.25	3	0.18(1)	8.6
Na1	32f	0.221(1)	0.221(1)	0.221(1)	4	0.125	4

$R_{wp} = 4.1\%$ ,  $R_{exp} = 3.7\%$ ,  $\chi^2 = 1.3$ ,  $R_B = 2.6$

atom	site	x	y	z	$B_{iso}$ (Å <sup>2</sup> )	sof	atoms per unit cell
Fe1	4a	0	0	0	1.4	1	4
Fe2	4b	½	0	0	1.4	1	4
N1	24e	0.307(3)	0	0	1.4	1	24
C1	24e	0.193(4)	0	0	1.4	1	24
O1	8c	0.25	0.25	0.25	3	0.60(1)	4.8
O2	48g	0.481(5)	0.25	0.25	1	0.12(1)	5.8
Na1	32f	0.214(2)	0.214(2)	0.214(2)	1	0.0625	2

atom	sites	x	y	z	$B_{iso}$ (Å <sup>2</sup> )	sof	atoms per unit cell
Fe1	4a	0	0	0	1	1	4
Fe2	4b	0.5	0	0	1	1	4
N1	24e	0.305(4)	0	0	1	1	24
C1	24e	0.192(5)	0	0	1	1	24
O1	48g	0.312(6)	0.25	0.25	3	0.029(2)	1.4

$R_{wp} = 3.6\%$ ,  $R_{exp} = 4.0\%$ ,  $\chi^2 = 0.8$ ,  $R_B = 1.5$

\*The  $\chi^2$  values below 1 are attributed to overestimated standard uncertainties for the data.<sup>7</sup>

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