

Supporting Information

NaSICON NaFe₂PO₄(SO₄)₂ revisited: insights on crystal structure and electrochemical performance

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Table S1. Cell parameters, obtained from Rietveld refinement of the XRD patterns collected for the 3 samples obtained from different precursors using solid-state reaction (N and AC samples) and using an ionothermal reaction (iN sample). The unit cell is described in the $R-3c$ (#167) space group.

Sample	Cell parameters of $\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$				Crystallite size, nm
	a , Å	c , Å	V , Å ³	V/Z , Å ³	
N	8.4138(3)	22.0392(6)	1351.19(5)	225.20(5)	80
iN	8.4651(6)	21.977(1)	1363.8(1)	228.1(1)	230
AC	8.4406(5)	22.0044(8)	1357.6(1)	226.3(1)	120
$\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$ by Ben Yahia <i>et al.</i> ¹ ($R-3c$ S.G.)	8.4243(7)	21.9728(16)	1350.47(18)	225.08(2)	

Table S2. ICP-OES results for the two almost pure samples of NFPS (based on XRD): samples N and AC, obtained via dissolution of precursors and solid-state synthesis with an annealing at 530°C.

	Expected stoichiometry of NFPS	Experimental compositions of samples, normalized by P content	
		N	AC
Na	1	1.07±0.03	1.08±0.02
Fe	2	1.99±0.03	2.04±0.02
S	2	1.99±0.03	1.92±0.02

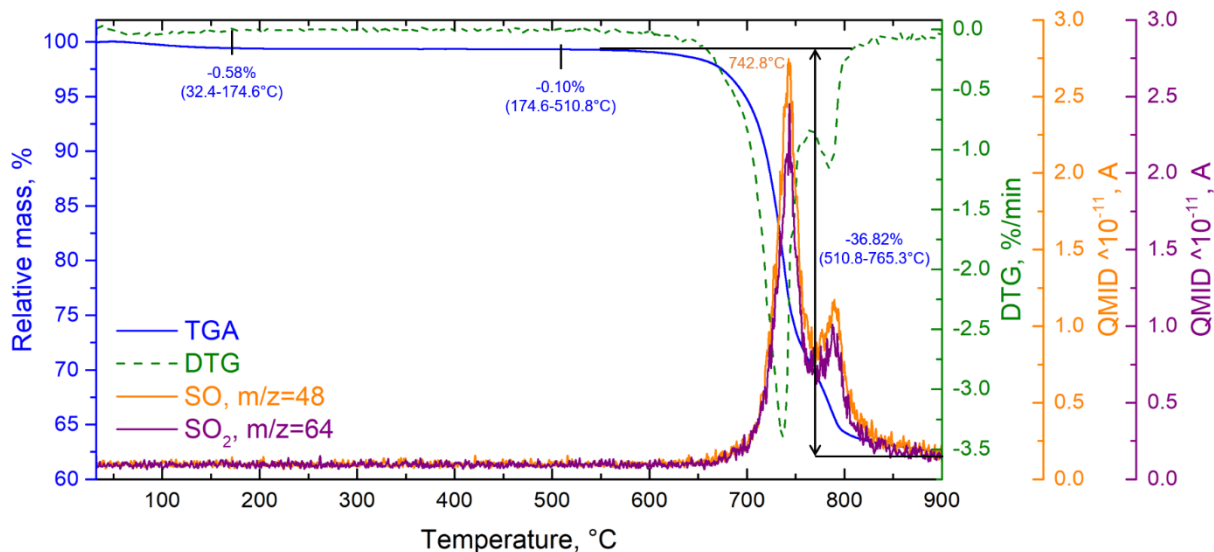


Figure S1. Thermogram of the sample N (blue curve) in combination with its derivative (dashed green curve), combined with mass spectrometry of SO and SO₂ evolving gases (orange and purple lines, respectively) in temperature range of 33-900°C under air.

Table S3. Structure refinement parameters of $\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$ in **R-3** S.G. (from **neutron** and **X-Ray** powder diffraction data).

Diffraction	Neutron	X-Ray
Chemical composition	$\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$	
Chemical formula weight	421.6	
Crystal system, space group	Rhombohedral, <i>R</i> -3 (#148)	
a , Å	8.4138(3)	
c , Å	22.0392(6)	
α , β , γ , °	90, 90, 120	
V , Å ³	1351.19(5)	
Z	6	
Calculated density, $\text{g}\cdot\text{cm}^{-3}$	3.131	
Radiation λ , Å	1.59	0.7093/0.7135
2θ range, °	13.000–146.00	2-40
Number of points	2381	1900
Number of observed reflections	552	284
Refined parameters	92	
R_B	0.018	0.029
R_w , R_{wp}	0.023, 0.021	0.038, 0.038
GOF	1.77	

Table S4. Selected interatomic distances of NFPS, as well as the average interatomic distance (Avg.) and the bond valence sum (BVS) as determined from the refinement in **R-3** S.G.

Na1-O3 2.512(2) × 6 Avg. 2.512(2) BVS 0.88(2)	Na2-O4 2.51(1) O4 2.69(3) O4 2.84(3)
Fe1-O2 1.983(2) × 3 O4 2.001(3) × 3 Avg. 1.992(3) BVS 3.2(3)	O4 2.54(1) O4 2.35(4) O4 2.16(3) Avg. 2.52(4) BVS 1.08(4)
Fe2-O1 1.990(3) × 3 O3 2.002(2) × 3 Avg. 1.996(3) BVS 3.16(3)	
S1/P1-O1 1.443(5) O2 1.457(1) O3 1.499(2) O4 1.497(2) Avg. 1.474(5)	

Bond valence sum for each atom was calculated based on the formula $S_{A-X} = \exp\left(\frac{R_0 - R}{b}\right)$, where A and X are the atoms forming the bond, R_0 the distance A-X which is an empirical parameter, and b (also an empirical parameter), which is usually fixed at $0.37 \text{ \AA}^{3.4}$. Following R_0 distances were used: $R_0(\text{Na}^+ - \text{O}) = 1.756 \text{ \AA}$, $R_0(\text{Fe}^{3+} - \text{O}) = 1.759 \text{ \AA}$.

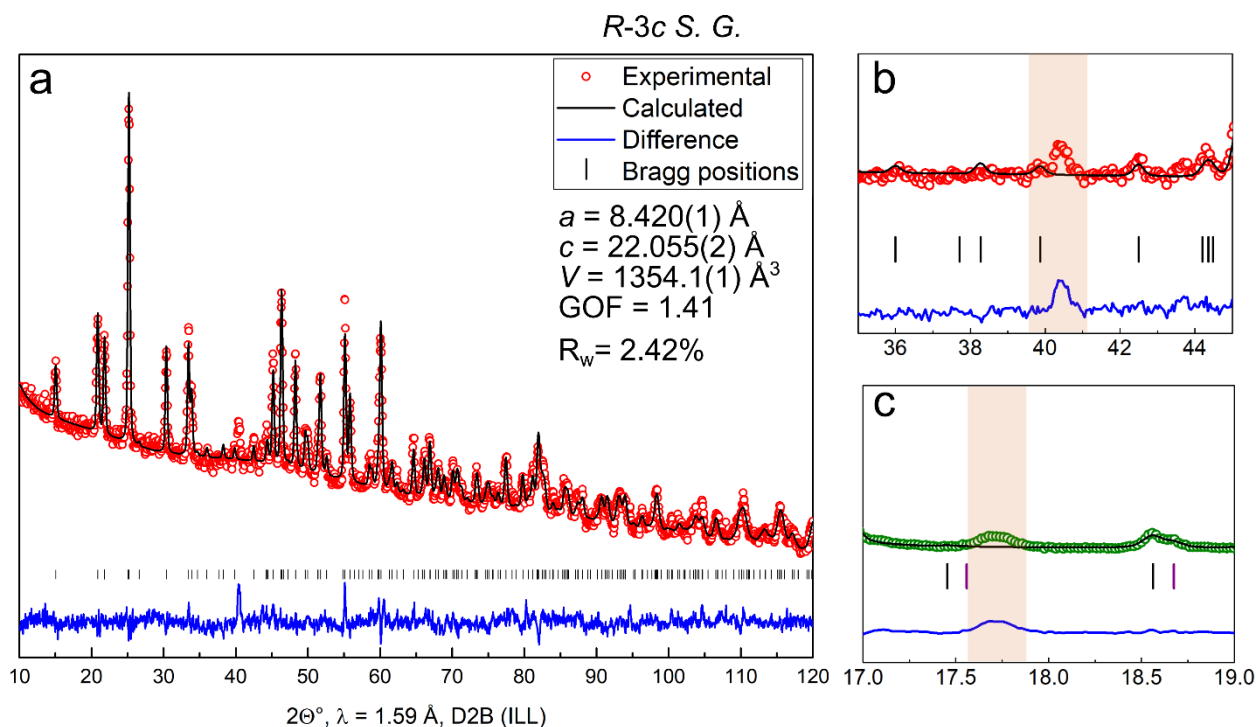


Figure S2. (a) Rietveld refinement of the NFPS NPD pattern in *R-3c S.G.* with (b) zoom of NPD pattern to highlight not described peak and (c) zoom of XRD pattern with the same non-indexed peak in *R-3c S.G.*

The refinement of the neutron diffraction data in the *R-3c S.G.*, as shown in **Figure S2** and in **Table S5**, provides slightly higher reliability factors and worse fit of the pattern, than in *R-3 S.G.* As mentioned before, the controversial peak 303 is not calculated, on the contrary to the results, obtained when the refinement is done considering a unit cell described in the *R-3 S.G.* (**Figure 3b,c**). Furthermore, high values were obtained for the atomic displacement parameters U_{iso} of P/S and O2 (*i.e.* $0.043(7) \text{ \AA}^2$ and $0.029(4) \text{ \AA}^2$, respectively), suggesting that their localization was not optimal. A significant Na deficiency was also calculated on the Na site ($0.672(2)$ instead of 1, with a fixed U_{iso} of 0.002 \AA^2 , or an occupancy of 1 with a huge U_{iso} of $0.052(6) \text{ \AA}^2$), and this one is not in agreement at all with the stoichiometry proposed by ICP-OES analyses and would impose for iron an oxidation state higher than 3. Note that Singh *et al.* reported also in 2024 for $\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$ a NaSICON structure described in the *R-3c* space group and showing a Na deficiency of $0.16(3) \text{ Na}^+$ per formula unit by refinement of neutron diffraction pattern, noting this non-indexed small intensity peak and suggesting that it comes from an impurity ².

Table S5. Structural parameters determined for $\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$, when its structure is described in the *R-3c* S.G. (from **neutron** powder diffraction data).

$\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$						
Atom	Site	x/a	y/b	z/c	$U_{\text{iso}}, \text{\AA}^2$	Occupancy
Na1	6 <i>b</i>	0	0	0	0.002	0.672(2)
Fe1	12 <i>c</i>	0	0	0.1477(2)	0.006	1
S1	18 <i>e</i>	0.2910(6)	0	0.25	0.043(7)	0.667
P1	18 <i>e</i>	0.2910(6)	0	0.25	0.043(7)	0.334
O1	36 <i>f</i>	0.0282(6)	0.2087(6)	0.1944(2)	0.0173(3)	1
O2	36 <i>f</i>	0.1923(6)	0.1700(6)	0.0885(2)	0.029(4)	1

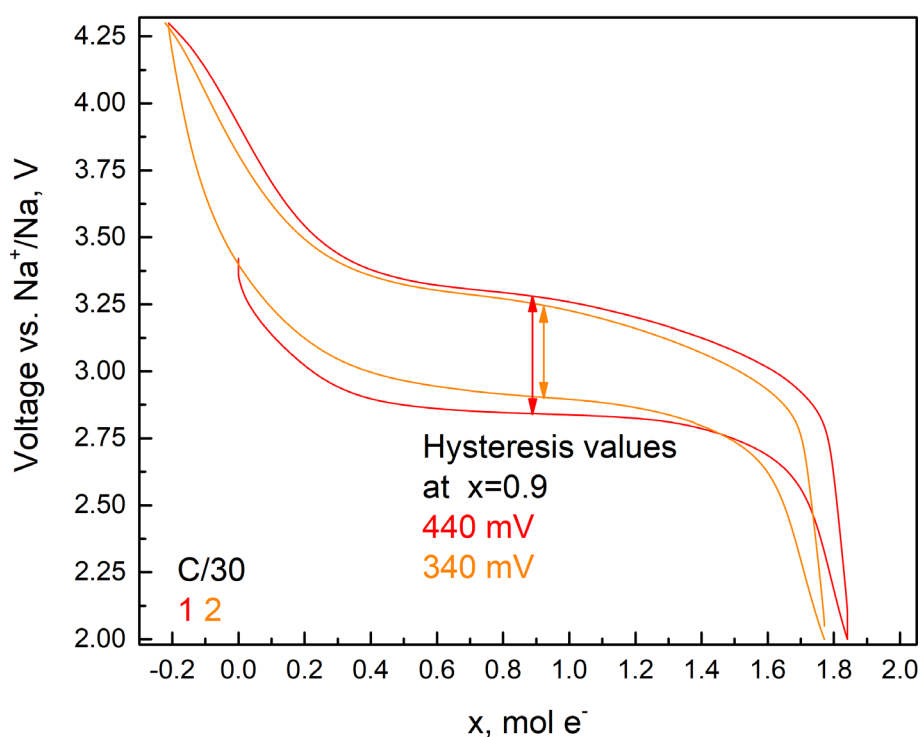


Figure S3. Comparison of voltage curves as a function of x during 1st (red) and 2nd (orange) cycles, x meaning mol of transferred electrons at cycling rates D/30-C/30. The hysteresis value is calculated at mid-value of x .

References:

- (1) Ben Yahia, H.; Essehli, R.; Amin, R.; Boulahya, K.; Okumura, T.; Belharouak, I. Sodium Intercalation in the Phosphosulfate Cathode $\text{NaFe}_2(\text{PO}_4)(\text{SO}_4)_2$. *J. Power Sources* 2018, 382, 144–151. <https://doi.org/10.1016/j.jpowsour.2018.02.021>.
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